THE NICKEL BULLETIN

A MONTHLY SUMMARY OF CURRENT INFORMATION

AUGUST, 1958

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ABSTRACTS OF CURRENT PUBLISHED INFORMATION ON NICKEL AND ITS ALLOYS

GENERAL

Thermal Properties of Metals and Alloys: Reference Data

C. F. LUCKS and H. W. DEEM: 'Thermal Properties of Thirteen Metals.'

Amer. Soc. Testing Materials Special Tech. Publn. 227, 1958; 29 pp. Price $1.25.

Recent technological developments give rise to many heat-transfer problems which involve utilization of the thermal properties of metallic materials. Thermal conductivity, thermal expansion, specific heat and density are frequently of importance: thermal diffusivity (which may be calculated from thermal conductivity, specific heat and density) is also in some cases significant. Since relevant data are insufficient for current requirements, Battelle Memorial Institute has carried out research, on behalf of Wright Air Development Center, to provide a fuller supply of accurate reference information. This publication contains results of experimental determinations made during that programme, correlated with values from the literature: the materials and temperature ranges for which values are recorded are indicated below. Unless otherwise shown, the following properties were determined over the full temperature range given: thermal conductivity, linear thermal expansion, specific heat, density and thermal diffusivity.

	Temperature Range	
	°F.	°C.
Aluminium (two types)	−250 to 800	−156·5 to 426·5
Chromium	75 to 3000	26 to 1648
thermal conductivity	400 to 1800	204 to 982
Copper	75 to 1900	26 to 1038
density	75 to 3000	26 to 1648
'Inconel' } 'Inconel X' }	−250 to 1800	−156·8 to 982
Magnesium	−250 to 600	−156·5 to 315·5
Molybdenum	75 to 3000	26 to 1648
thermal conductivity and diffusivity	400 to 1600	204·5 to 871
'K Monel'	−250 to 1800	−156·5 to 982
Carbon steel (SAE 1010)	−250 to 1650	−156·5 to 899
Stainless steels 17–7 } 18–8–Mo } 18–8–Nb }	−250 to 1800	−156·5 to 982

Testing of Metals

The 1958 Report of the American Society for Testing Materials Committee E-1 on Methods of Testing recommends the following methods:

'Determination of Poisson's Ratio at Room Temperature.' (Tentative)

Amer. Soc. Testing Materials, Preprint 58, June 1958, pp. 21–4.

The schedule covers apparatus, specimens, and procedures for the determination of Poisson's ratio from tension tests of structural materials at room temperature. The method is limited to specimens of rectangular section and to materials in which creep is negligible compared with the strain produced immediately upon loading. *Poisson's ratio* is defined as 'the absolute value of the ratio of transverse strain to the corresponding axial strain for uniformly distributed axial stresses below the proportional limit of the material'.

'Revised Definitions of Terms Relating to Methods of Mechanical Testing' (Tentative)
ibid., pp. 25–31.

The terms proposed are classified in sections relating, respectively, to (1) general definitions associated with testing of mechanical properties, (2) tension, compression, hardness, shear and torsion testing, (3) fatigue testing, (4) bend testing. An appendix contains a list of symbols which are frequently used in lieu of, or together with, the terms covered in the schedule.

'Revised Standard Hardness Conversion Tables for Metals: Relationship between Brinell Hardness, Diamond Pyramid Hardness, Rockwell Hardness and Rockwell Superficial Hardness',
ibid., pp. 32–9.

The tables and letterpress of the proposed revision embody data on the hardness relationships, on the various scales, for (1) carbon, alloy and tool steels, (2) nickel and high-nickel alloys, (3) cartridge brass. Methods of hardness testing, the principle of conversion used, and the significance of hardness tests are discussed, also methods of reporting results.

Non-Destructive Testing of Metallic Materials

'Symposium on Non-Destructive Tests in the Field of Nuclear Energy.'

Published by *Amer. Soc. Testing Materials*, 1958. *Special Tech. Publn.* 223; 395 pp.

The symposium (held in April 1957) was jointly

sponsored by the following organizations, the aims and activities of which are briefly summarized as a preface to the report:

American Institute of Chemical Engineers, Nuclear Engineering Division

American Nuclear Society

Atomic Industrial Forum, Inc.

Society for Non-Destructive Testing, Inc.

American Society for Testing Materials

The meeting resulted from consideration, by a committee of the U.S. Atomic Energy Commission, of the large amount of information which had been accumulated, in the form of confidential reports, in the course of work carried out in various laboratories and other establishments operating under A.E.C. sponsorship. Declassification of many such reports led to the proposal that a symposium should be held at which the information contained in them could be brought to the notice of a wider circle of research workers and industrialists to whom it would be of practical value. The object of the symposium was therefore 'to disseminate fifteen years of research and development in the non-destructive testing applications in the nuclear field and to reach people interested in nuclear and industrial applications.'

The scope of the material presented is indicated below, with note of papers which contain specific reference to use of the methods described for examination of nickel-containing materials.

Section I. Four Survey and Educational Lectures,

serving as introduction to the broad principles of eddy-current and ultrasonic testing methods and radiation techniques. Tests of these and other types are described in detail in later sections, in relation to their use in examining reactor components and fuel assemblies.

Section II. Testing of Reactor Components, Ultrasonic Methods of Test,

including

R. B. OLIVER, R. W. McCLUNG and J. K. WHITE: 'Production Inspection of Pipe and Tubing by the Immersed Ultrasonic Method', pp. 62–78; disc. p. 79.

Report on experience at Oak Ridge National Laboratory, in inspection-testing of tubing of various sizes, using the 'Immerscope', an instrument which provides for either contact scanning or immersed scanning. This method of defect detection has been applied to tubing of various materials, including 'Hastelloy B' and 'Inconel'.

W. R. PLANT and C. MANNAL: 'An Eddy-Current Test for Capillary Tubing', pp. 80–7.

Small-diameter seamless stainless-steel tubing produced by General Electric Company for nuclear-plant applications is subjected, in all cases, to a rigorous hydrostatic-pressure test, but there appeared to be some possibility that certain batches might contain short, relatively deep defects which would not be revealed by that method of inspection. It was therefore required that an even more discriminating method of examination should be found which would give rapid results, in terms free from the possibility of ambiguous interpretation. This paper describes a method developed at Knolls Atomic Power Laboratory, and records results of its application to 0·05-in. (0·125-cm.) o.d. tubing in two types of austenitic stainless steel.

J. W. ALLEN and R. B. OLIVER: 'Inspection of Small-Diameter Tubing by Eddy-Current Methods', pp. 88–109; disc., pp. 110–11.

Notes on the essential features of eddy-current test technique, and the specific problems involved in application of the method to testing of small-diameter tubing. Description of the 'Cyclograph' and the 'Impedograph', two instruments devised, for this purpose, at Oak Ridge National Laboratory. The use of the instruments is demonstrated by reference to tests on 'Nimonic 80', 'Hastelloy B' and 'Inconel'.

R. C. ROBINSON: 'A Non-Destructive Test for Intergranular Corrosion in Stainless Steel', pp. 112–18.

Description of eddy-current equipment and test technique for determination of susceptibility to intergranular corrosion of unstabilized chromium-nickel steel of the 18-8 type. Test developed by Du Pont de Nemours and Company.

R. B. OLIVER, G. M. TOLSON and A. TABOADA: 'The Use of Penetrants for Inspection of Small-Diameter Tubing', pp. 127–39; disc., pp. 140–1.

Discussion of the advantages and limitations of liquid-penetrant methods of inspection, and of the scope of usefulness of contrast- and fluorescent-penetrant techniques. Step-by-step account of the essential features of penetrant testing, followed by account of fluorescent-penetrant procedure developed at Oak Ridge National Laboratory for testing small-diameter tubing. Experimental data supporting the description include tests on 'Inconel' tubing.

J. W. ALLEN, R. A. NANCE and R. B. OLIVER: 'Eddy-Current Measurement of Clad Thickness', pp. 201–12; disc., p. 213.

Oak Ridge National Laboratory has under way an inspection programme designed to determine the quality of fuel plates in one of the U.S. A.E.C. reactors. These plates usually consist of a thin uranium-aluminium-alloy core clad with a corrosion-resistant metal having good heat-transfer properties. Minimum cladding thickness must be adequate (1) to prevent radioactive contamination of the reactor system and its surroundings by the fuel and the isotopes produced by fission, and (2) to protect the fuel-bearing alloy from the corrosive action of the reactor coolant. A non-destructive method which will ensure that the core is sufficiently well clad is therefore essential. Thickness measurement by ultrasonic resonance was not feasible, but success has been achieved by an eddy-current procedure, which is described in this paper. As an introduction to the report on the specific method used, the authors discuss the principles of induced

eddy currents. The supporting data include measurements of thickness of cladding on aluminium-clad uranium and 'Inconel'-clad copper.

III. Testing of Fuel Assemblies,

including

L. H. COOK: 'Nickel Thickness Gauge', pp. 225–30.

Determination of thickness of nickel films by measurement of the force required to pull a small magnet from the surface is apt to give inconsistent and unreliable results if the film is extremely thin and/or the surface is rough. The magnetic characteristics of nickel are such as to make possible utilization of a reluctance technique, and this is the principle employed in the instrument described in the present paper. It is claimed that the thickness of nickel foils 0·0001–0·0006 in. (0·0025–0·015 mm.), supported on aluminium, brass, and copper, can be measured with 10 per cent. accuracy.

IV. Miscellaneous Subjects Related to Non-Destructive Testing in the Field of Nuclear Energy,

including

G. D. LINSEY and H. L. LIBBY: 'Nickel Depth Meter', pp. 344–51.

Magnetic methods of measuring the thickness of thick layers of nickel have certain limitations, and, in cases where the conductivity and permeability of the base metal differ from those of nickel, electromagnetic techniques based on eddy currents offer some advantages. This paper describes an instrument which utilizes this principle. It is claimed to be capable of measuring thickness of nickel over a range of 0·1 to 2·0 mils. Under ideal conditions accuracy is within 5 per cent., varying with the uniformity of the electrical characteristics of the nickel and of the base material.

NICKEL

Electrorefining of Nickel: New Inco Process

L. S. RENZONI, R. C. McQUIRE and W. V. BARKER: 'Direct Electrorefining of Nickel Matte.'

Jnl. of Metals, 1958, vol. 10, June, pp. 414–18.

In a paper presented at the 1958 Annual Meeting of the American Institute of Mining, Metallurgical and Petroleum Engineers the authors gave a detailed account of work, by The International Nickel Company of Canada, Ltd., which culminated in development of a modified process regarded as revolutionary in the field of electrorefining. The original paper was abstracted in *Nickel Bulletin*, 1958, vol. 31, No. 6, pp. 155–6. This version is an abridgement of that paper.

The new procedure by-passes all the traditional high-temperature operations involved in preparation of metallic nickel anodes, and employs sulphide anodes, which are cast directly from the Bessemer matte. The process has the additional advantage of making possible recovery of elemental sulphur, selenium and cobalt.

Chemisorption of Nitrogen on Nickel

R. J. KOKES and P. H. EMMETT: 'Chemisorption of Nitrogen on Nickel Catalysts.'

Jnl. Amer. Chemical Soc., 1958, vol. 80, May 5, pp. 2082–6.

It has been shown in earlier investigations that on thin metal films considerable chemisorption occurs at −195°C., but this effect has not previously been reported for nickel catalysts formed by reduction of the oxide. In view of the wide use made of nitrogen adsorption at −195°C. for measuring the surface area of metals and other solids, it appeared desirable to ascertain whether chemisorption of nitrogen occurred at that temperature.

The work described in the present paper showed that both pure nickel catalysts and those promoted with small amounts of silica will chemisorb nitrogen to a slight extent at about 250°–300°C. and that, at least in the case of pure nickel catalysts, a different type of chemisorption occurs at −195°C. For the pure nickel catalyst the amounts chemisorbed at high temperatures correspond to 5 per cent. surface coverage calculated as molecular nitrogen: the low-temperature chemisorption corresponds to as much as 28 per cent. surface coverage. The nitrogen adsorbed at −195°C. is easily removed by evacuation at room temperature and is almost completely blocked out by the presence of the chemisorbed nitrogen put on at high temperatures. The amount of nitrogen adsorbed at −195°C., expressed as a fractional surface coverage, is very sensitive to the previous history of the catalyst.

Adsorption of Hydrogen on Nickel-Kieselguhr Catalyst

L. LEIBOWITZ, M. J. D. LOW and H. A. TAYLOR: 'The Adsorption of Hydrogen on Nickel-Kieselguhr.'

Jnl. Physical Chemistry, 1958, vol. 62, Apr., pp. 471–8.

Rates of adsorption were studied over a pressure range from about 1 cm. to 1 atm., at temperatures from 160° to 325°C. Some of the observations made are considered to cast some doubt on classical interpretations of chemisorption.

Effect of Neutron Irradiation on Properties of Nickel

M. J. MAKIN: 'The Effect of Neutron Irradiation on the Mechanical Properties of Copper and Nickel.'

Jnl. Inst. Metals, 1957–58, vol. 86, June, pp. 449–55.

Report of tests on wire specimens of commercially pure metals. The effect of neutron irradiation at 100°C. with 5×10^{19} neutrons/cm.^{2}, on the mechanical properties of annealed wire of copper and nickel, was studied at several temperatures between −195° and +200°C. Irradiation caused an increase in yield stress of both metals; the effect was markedly temperature-dependent, being very much greater

at low temperatures than at higher levels: this temperature-dependent rise in yield stress was reversible and was not due to thermal annealing. Rate of work hardening, especially at low strains, was greatly reduced by irradiation. Increase in ultimate tensile strength resulting from irradiation was much less than the change occurring in yield stress. Large reduction in elongation-to-fracture resulted from irradiation.

It is observed that the activation energy of the thermally activated process responsible for the onset of plastic flow in irradiated metal is not a constant, but increases with falling temperature in a manner similar to that observed with materials showing marked yield-point phenomena due to strain-ageing. However, because of the large effect upon the whole stress/strain curve and the constancy of the yield characteristics over a wide temperature range, the whole effect cannot be attributed to atmospheres of point defects around the dislocations. It is considered more probable that the hardening is due either to the formation of 'jogs' on dislocations by the condensation of point defects or to the presence of small planar clusters of interstitial atoms or vacancies.

Testing of Metals

See abstract on p. 211.

Non-Destructive Testing of Metallic Materials

See abstract on p. 211.

Creep of Nickel

See abstract on p. 231.

Coupling of Nickel Materials with Graphite: Effect on Corrosion-Resistance

See abstract on p. 245.

Chromatographic/Spectrophotometric Determination of Nickel and other Metals

W. J. FRIERSON, D. A. REARICK and J. H. YOE: 'Separation by Paper Chromatography and Spectrophotometric Determination of Trace Amounts of Cobalt, Nickel, Copper, and Zinc.'

Analytical Chemistry, 1958, vol. 30, Apr., pp. 468–71.

Details are given of a method involving a two-solvent chromatographic separation of the ions of all four of the elements mentioned, followed by sensitive and rapid photometric determination. The procedure is applicable to any combination of the four elements.

Estimation of Nickel in Biological Material

L. M. PROVOTOROVA: 'Application of Chromatography in Forensic Determination of Nickel in Biological Material.'

Aptechnoe Delo, 1957, vol. 6, No. 3, pp. 28–32.

Full details of the recommended method are given in *Chemical Abstracts*, 1958, vol. 52, pp. 6062–3.

Determination of Nickel in Copper Alloys

See abstract on p. 222.

Determination of Nickel in Titanium Alloys

See abstract on p. 223.

Nickel Catalysts in the Petroleum Industry

P. D. WILMOT: 'Nickel and Cobalt Catalysts in the Petroleum Industry.'

Petroleum, 1958, vol. 21, June, pp. 187–190, 200; July, pp. 225–8, 254.

This article, published in two parts, describes what is known of the structure and surface mechanisms of catalysts of the iron group which are of importance to the petroleum and related industries. Comparisons of the catalytic behaviour of iron, cobalt and nickel are drawn from a wide range of applications, with emphasis on the last two metals.

An introductory section briefly outlines the current state of knowledge of the basic principles of catalysis: relations between catalytic activity and vacancies in the electronic *d* levels of the metals are emphasized. An account is given of the production of hydrocarbons by the Fischer-Tropsch synthesis and it pointed out that both skeletal iron and skeletal nickel catalysts are active for that synthesis, even though the nickel is normally a very active hydrogenation catalyst. Current views of the mechanism of the process favour the intermediate formation of alcohols. The Fischer-Tropsch process uses as raw material $CO+H_2$, but olefines also may be polymerized by means of nickel oxide on silica-alumina or cobalt on charcoal: it is suggested that this reaction is carried out by means of an acid-type mechanism. The first part of the paper concludes with an account of the production of synthesis gas from hydrocarbons and steam. A possible surface mechanism for this type of reaction is indicated.

Part 2 discusses the types of surface reaction which may be occurring in the hydrogenation of double bonds: it is pointed out that the mechanisms are far more complex than has been commonly supposed. Recent developments in the petroleum industry, in the partial hydrogenation of di-olefines to mono-olefines, are also studied. It is suggested that nickel subsulphide, which is an effective catalyst in this connexion, operates by functioning as an *n*-type semi-conductor. The structure and the surface mechanism of a nickel/silica-alumina catalyst, for the isomerization of *n*-octane to *iso*-octane is next discussed. It is suggested that the carbonium-ion mechanism which is thought to be responsible for the normal cracking action of silica-alumina operates in this case also. The presence of the nickel modifies this mechanism. Desulphurization techniques are discussed at some length, and the activities of nickel/tungsten-sulphide and cobalt/molybdenum-oxide are compared. The author favours the view that in the desulphurization of mineral oils the sulphur in the thiophene compounds is attacked at different sites from those at which hydrogenation of the

double bonds of these compounds occurs. The paper ends with an account of the activity of nickel/calcium-phosphate as a dehydrogenation catalyst in the conversion of butylene to butadiene.

Welding of Nickel for Chemical Plant

See abstract on p. 250.

Heat of Formation of Nickel Carbonyl

K. W. SYKES: 'Heat of Formation of Nickel Carbonyl from Combustion Calorimetry.'

Jnl. Chemical Soc., 1958, May, pp. 2053–4.

Short note on investigation of discrepancies between recently reported values for heat of formation of nickel carbonyl. It is considered likely that the true value lies between 36 and 40 kcal. per mole^{-1}.

ELECTRODEPOSITION AND OTHER COATING METHODS

Productivity in Metal Finishing

'A Review of Productivity in Metal Finishing.' Published by *British Productivity Council*, June 1958; 32 pp.

The report is one of a series prepared by teams of British industrialists who, in 1950, visited the U.S.A. under the technical assistance programme of the Economic Co-operation Administration. It deals with progress in the Metal Finishing Industry in Britain since that date, with particular reference to some of the recommendations made, at that stage, by the team which visited America. In view of the impossibility of making a complete survey of so wide a field, the scope of the present report is confined to the two major branches investigated by the British team in the U.S.A., *viz.*, organic finishes and electrodeposition.

The report opens with the following note, urging the vital significance of a high standard of quality in all types of metal finishing.

> 'The importance of a high standard of metal finishing may appear obvious, but it cannot be over-emphasized. As the team stated: 'There is no doubt that, whilst the general public may not appreciate the nature of the processes by which a finish is produced, it is quick to assess whether the result is decorative. Equally, the effectiveness of the finish as a corrosion preventative is of vital importance and in the long run it is by the durability of the product in service that the reputation of the manufacturer is judged'.'

This introduction is followed by consideration of the structure of the metal-finishing industry, recent progress in plant and techniques, and the extent to which there is adequate appreciation of the need for higher quality in finished products.

The chapter on organic finishes covers types of paint, methods of application (with special reference to mechanized procedures, spraying techniques and other methods of application), drying, and inspection.

The Team consider that in **Electrodeposition,** with which the next chapter deals, much progress has been made since 1950. The standards of the industry still vary widely from plant to plant: although in many plants production is organized on lines which permit smooth and consistent output of high-quality products, in others there is ample room for more careful analysis of operational requirements and for modification in methods.

Among the comments made are the following:

> 'It is in the increasing use of bright and semi-bright plating solutions that possibly the most noticeable advances have been made in Britain in the last few years. Chromium over nickel is the material most widely used for decorative purposes. The chromium film is thin and has no very great protective property in itself, serving only to impart a tarnish-resisting surface to the finish. Before chromium plating, therefore, the article receives a deposit of nickel, and it is here that the greatest difficulty in the post-war years has been experienced. Nickel has been and remains scarce . . . There is no doubt that the thickness applied has sometimes been skimped, with poor results.' (In this connexion see note below.

The authors of the Productivity Report draw attention to the advantages of bright and semi-bright nickel solutions, with notes as to the need for specially careful control of the bright baths, in order to minimize brittleness, which may give rise to cracking of a coated component when flexed.

Other aspects of progress in the electroplating industry to which summary reference is made include plating with alloys (e.g., tin-nickel and brass), periodic-reverse plating, polishing (at both the pre-plating and the finished stages) and processing methods and control.

The comment is made that 'the most noticeable shortcoming in the plating industry (with, of course, many exceptions) is the lack of precise process control.' It is urged that work study, which has as yet hardly been introduced in this industry, is urgently required, and would, if systematically employed, help to raise efficiency in all branches and aid the output of consistently high-grade products.

The report notes that in recent years great improvement has been made in plant and equipment: some typical modern plant is illustrated and details are given of seven representative firms who are employing metal-finishing equipment of modern type, under efficient operating conditions.

Note: *There is now no shortage of nickel for plating or any other application*, and it is therefore possible to ensure that in all cases adequate undercoats of nickel are used.) For particulars of the thicknesses necessary to ensure satisfactory behaviour in various types of outdoor and indoor service conditions, attention may be directed to *British Standard Specification* 1224,

which covers requirements for nickel coatings on steel, copper or copper-alloy, and zinc or zinc-alloy bases.

A recent revision of that specification (which has already been circulated to industry and will shortly be issued as Standard) embodies some significant changes which have become necessary because a demand has arisen for even thicker coatings of nickel, and because new and improved methods for testing the coatings have become available. The essential difference between the new specification and the 1953 edition of *B.S.* 1224 is the use of the SO_2 test and the acetic-acid/salt-spray test, in place of the salt-spray test, for determining the corrosion-resistance of the plated parts.

Important changes have been made in the thickness requirements. In *B.S.* 1224: 1953 there were four grades, Ni12S, Ni8S, Ni4S and Ni2S. (The numbers in the classification code refer to minimum thickness of nickel deposit, in thousandths of an inch, i.e., Ni12S refers to coatings 0·0012 in. thick.) In the new draft the grade Ni2S has been withdrawn, and the three remaining grades are suggested, respectively, for 'severe', 'moderate' and 'mild' duty. In addition to these grades, a further classification, Ni12SD, covers a thickness of 0·0012 in. of buffed ductile semi-bright nickel, or a minimum of 0·0003 in. of copper, + a minimum of 0·001 in. of ductile nickel, one of the coatings being buffed.

A test procedure for determining the ductility of the nickel deposit by bending a plated strip over a mandrel with a radius of 0·045 in. is recommended.

For nickel on copper or brass two classifications, Ni6C and Ni3C, are recommended, for 'severe' and 'moderate' duty, respectively. (Classifications in the earlier specification were Ni5C, Ni3C and Ni1C.)

For nickel coatings on zinc-base-alloy die castings the two original grades, Ni6Z and Ni3Z, are replaced by three grades, Ni10Z, Ni6Z and Ni3Z, recommended respectively for 'severe', 'moderate' and 'mild' duty.

In addition to the above requirements, clauses have been introduced to provide for the possibility of measurement of thickness of nickel at any position on the plated component, by tests to be agreed upon between supplier and purchaser.

Specification of Nickel Plating for Decorative Applications

H. C. CASTELL: 'The Value of Specifications in Decorative Nickel Plating.'

Metal Finishing Jnl., 1958, vol. 4, Apr., pp. 119–21.

The article is designed to explain the causes of variations in behaviour of nickel and nickel/chromium coatings, as resulting from the adequacy or the inadequacy of the plating technique used, with particular reference to the thickness of the coatings deposited.

It is pointed out that for many years it was believed that an electrodeposited metal was intrinsically

Basis Metal	Service	Minimum Thickness of Nickel Deposit	
		in.	mm.
Steel	Severe exterior service (e.g., parts of a car which might be attacked by road salt and exhaust fumes)	0·002–0·003	0·05–0·075
Steel	General exterior and severe internal service (e.g., external parts on cars, kitchen and bathroom ware)	0·001–0·0015	0·025–0·0375
Steel	Interior service where warm, dry atmospheres are normally obtained	0·0005–0·001	0·0125–0·025
Brass	Exterior service or severe interior service	0·0005–0·0007	0·0125–0·0175
Brass	Interior service with warm and dry atmospheres	0·0003–0·0005	0·0075–0·0125
Zinc-base die castings*	Exterior service or severe interior service	0·001–0·0015 (with 0·0003 copper undercoat)	0·025–0·0375 (0·0075)
Zinc-base die castings*	Interior service with warm and dry atmospheres	0·0005–0·0007 (with 0·0003 copper undercoat)	0·0125–0·0175 (0·0075)

* It should be noted that in the case of zinc-base die castings the copper undercoat is regarded purely as a means of preventing attack by the acid nickel solution on the zinc alloy and formation of immersion deposits of nickel, *not* as a substitute for part of the nickel coat when it acts as a corrosion-preventive layer.

porous and that it was necessary to seal the holes in the initial layers by depositing a sufficient thickness of metal or by buffing the deposit and thus flowing metal over the holes. In later years, however, research has demonstrated that it is possible, by correct operating conditions, to produce sound deposits, but that it is still possible for premature failure to occur in certain coatings. Recent work has established that the true cause of breakdown is corrosion of the nickel deposit itself, in environments which are aggressive to the metal.

The main factors which contribute to early breakdown of nickel are

(1) ready-made pores and discontinuities, arising from co-deposition of insoluble particles suspended in solution,

(2) gas-bubble pitting,

(3) cracks in the deposit,

(4) penetration of the deposit by corrosion.

Factors 1 and 2 have been practically eliminated by improvements in plating technique and solutions: incidence of cracking is being lessened by use of stress-reducing agents and by constant purification of the electrolytes.

In study of the fourth possible cause of failure, it has been shown that time for penetration is largely a function of (*a*) the thickness of the nickel deposit, (*b*) the type of corroding agent with which the plated part is in contact, and (*c*) the form of the article, which affects uniformity of plating and ease of cleaning in service.

Exhaustive tests, made in the U.S.A. and in this country, have demonstrated conclusively that the thickness of nickel must be adequate for the type of atmosphere with which the part will come into contact and that the thickness needed varies according to the severity of the conditions. As a result of careful assessment of the data available, the specification shown on page 216 is recommended.

As an aid to ensuring uniformity of deposits in recessed areas, and on parts of difficult shape, carefully designed racking is strongly recommended.

Cleaning of Metal Surfaces for Electroplating

AMER. SOC. TESTING MATERIALS: 'Proposed Tentative Recommended Practice for Cleaning Metals Prior to Electroplating.'
Contained in Report of A.S.T.M. Committee B-8 on Electrodeposited Metal Coatings.
A.S.T.M. Preprint 14, June 1958, pp. 7–15.

It is emphasized that production of the degree of surface cleanliness essential for satisfactory coating requires the use of multi-stage cleaning cycles. This schedule makes recommendations for preparatory cleaning procedures, using: a solvent which will remove the bulk of the soil; intermediate cleaning, with alkaline media; final electrocleaning, to remove trace solids and adherent impurities; acid treatment and surface conditioning, to remove oxides which may be formed during the cleaning process, and to microetch the surface. In the introductory section of the schedule a review is made of the nature of the soil most likely to be present on surfaces which are being prepared for plating; of the characteristics of individual metals which call for consideration in preparing them and of criteria which may be used to assess cleanliness of surfaces.

Bright Nickel Plating: Review of Development and Present Status

D. J. FISHLOCK: 'Bright Nickel Plating. Part V. Brightening Agents.'
Product Finishing, 1958, vol. 11, June, pp. 65–75

This final article in a series appraising the present status of bright nickel plating reviews the present state of knowledge on brightening agents and the nature of the brightening action. It includes a useful table listing some British and U.S. patents on 'notable proprietary brighteners': the period covered is 1938–1955. The review closes with a consideration of the theories which have been advanced to explain the mechanism of brightening.

Electrodeposition of Nickel from Sulphamate Solutions

'Stress-free Nickel Plating.'
Metal Progress, 1958, vol. 73, Apr., pp. 90–1.

The article is based on a paper presented by R. C. BARRETT before a Branch of the American Electroplaters' Society. It gives a brief survey of the technique, and emphasizes the widening scope of applications in which the unusual properties of sulphamate deposits are being utilized. (Full details have been given in a fundamental report published by the same author in *Plating*, 1954, vol. 41: see abstract in *Nickel Bulletin*, 1954, vol. 27, No. 11, pp. 207–8.)

The main advantage of the sulphamate solutions is their ability to produce low-stress or stress-free nickel deposits without the aid of organic agents: by appropriate modification in the composition of the electrolyte, and in plating procedure, it is possible to vary the internal stress in the deposit from a low tensile value to a considerable compressive stress. Some of the applications in which this characteristic is usefully applied are briefly reviewed.

The basic composition for a general-purpose sulphamate plating bath which will deposit nickel of medium hardness (Vickers 250–350) is given as

	oz./gal.	*g./L.*
Nickel sulphamate	60	449
Nickel metal content	10·2	76·4
Boric acid	4	30
Anti-pitting agent	0·05	0·38

The bath is usually operated at pH 3–5, in the range 100°–140°F. (38°–60°C.). Maximum cathode current density is 300 amp./sq.ft. (32·5 amp./dm.^{2}) at 140°F. (60°C.).

Deposition of Nickel from Alkaline Solutions

E. B. SAUBESTRE: 'Alkaline Nickel Plating.'
Plating, 1958, vol. 45, May, pp. 479–85.

Of the many metals which are commercially electrodeposited, nickel and chromium only are almost never deposited from alkaline solutions, although, particularly in the case of nickel, several suitable complexes are known, and, in certain applications, alkaline electrolytes might offer certain advantages. A major limitation to such development is, however, the fact that deposits made from alkaline solutions are always highly stressed, and a further factor is that the type of electrolyte most generally used for alkaline plating, i.e., the cyanide bath, cannot be used for deposition of nickel.

The reasons for these limitations are discussed in detail in the present paper, and, on the basis of deposition-potential data and other considerations, it is shown that although caustic and cyanide solutions are impracticable, polyphosphates and ammonia are suitable inorganic complexing agents, whilst dibasic carboxylic acids, alpha-hydroxy carboxylic acids, alpha-amino acids and amines are suitable organic media. E.D.T.A. is not promising, and the use of the Ni^+ ion is not recommended.

In the second part of the discussion the author reviews some published data recording the use which has been made, in practice, of alkaline solutions for deposition of nickel. The types of solution considered, the conditions for their operation, and the results obtained, are briefly noted below.

(1) *Ammoniacal Solutions*

In work on the physical properties of nickel deposits made from various solutions, a bath of the following composition was used:

	g./L.
$NiSO_4.7H_2O$	210
$NiCl_2.6H_2O$	60
$(NH_4)_2SO_4$	50
pH (adjusted with NH_3)	8·5
Temperature (°C.)	25–80
Current density	
(amp./ft.²)	5–15
(amp./dm.²)	0·54–1·62

Hard, lustrous, brittle deposits were obtained.

Another alkaline bath reported was of the following compositions:

	g./L.
$NiSO_4.6H_2O$	400
$(NH_4)_2SO_4$	20
KCl	10
NH_4OH (25%)	25 *ml./L.*
pH	8 or more
Temperature (°C.)	20–35
Current density	
(amp./ft.²)	5–15
(amp./dm.²)	0·54–1·62

It was found necessary to include some chloride in order to ensure adequate corrosion of the anode. Lustrous, hard, but stressed deposits were produced.

(2) *Ammoniacal-Polyphosphate Solutions*

The 'Zialite' electrolyte, specially designed for deposition of nickel on zinc-base materials, is presumed, from patent literature, to be of approximately the following type:

	g./L.
$NiSO_4.6H_2O$	120
$Na_4P_2O_7.10H_2O$ (pyrophosphate)	65
$NaHSO_3$ (bisulphite)	2
$2Na_3C_6H_5O_7.11H_2O$ (citrate)	60
$C_6H_8O_7$ (citric acid)	15
NaCl	30
NH_4OH (28%)	30–60
pH	7·5–9·0
Temperature (°C.)	20–35
Current density	
(amp./ft.²)	2–20
(amp./dm.²)	0·22–2·16

The pyrophosphate not only complexes nickel, but probably acts also to reduce the dissolution of zinc by formation of insoluble zinc-phosphate coatings, while the citrate acts to complex the nickel in solution, thereby also reducing the tendency to form displacement coatings. Citrate may also act as a buffer. The bisulphite improves the throwing power, while the ammonia not only complexes nickel, but serves to adjust pH to the desired level.

(3) *Organic Complex Solutions*

A brief summary is made of the nature of two electrolytes (developed primarily for deposition of nickel on zinc) in which organic hydroxyacids such as citrates, tartrates and lactates were employed as complexing agents. In all cases, however, these solutions have been operated under slightly acid conditions. More recently, an alkaline organic-complex electrolyte has been proposed by Du Rose *et al* (*U.S. Pat.* 2,773,818). Two compositions are covered: see below.

	Solution No. 1	*Solution No.* 2
	g./L.	*g./L.*
$NiSO_4.6H_2O$	100	—
$NiCl_2.6H_2O$	—	85
$Ni(NO_3)_2$	20	20
NH_4Cl or NaCl	35	—
Na_2SO_4	—	75
$NaHSO_3$	5	5
$2Na_3C_6H_5O_7.11H_2O$ (citrate)	66	66
$N(CH_2)_2N.(CH_2COOH)_4$ (EDTA)	60	40
$N(CH_2.CH_2OH)_3$ (triethanolamine)	40 *ml./L.*	40 *ml./L.*
pH (adjusted with NaOH)	7(6·5–12)	7·5
Temperature (°C.)	60	60
Current density		
(amp./ft.²)	40	40
(amp./dm.²)	4·32	4·32

In both solutions the sulphate acts as the main source of nickel, chloride promotes anode corrosion and improves conductivity, ammonium salts improve lustre and ductility, nitrate represses evolution of hydrogen (permitting higher current densities), bisulphite improves throwing power, citrate acts as a complexing agent and buffer, and E.D.T.A. and triethanolamine function as complexing agents.

(4) *Alkaline Electroless Nickel Solution*

Brenner and Riddell, in 1946 and 1947, discussed an alkaline solution for deposition of nickel by the electroless process, and the composition suggested was later modified by Sullivan and Eigler for use in plating semi-conductors. (*Jnl. Electrochem. Soc.*, 1957, vol. 104, pp. 226–230: abstract in *Nickel Bulletin*, 1957, vol. 30, No. 7-8, p. 113). The present author has further adapted the solution, by eliminating the reducing agent (hypophosphite) required for electroless operation, and using current. The further modification has resulted in a solution of the following composition:

	g./L.
$NiCl_2.6H_2O$	30
NH_4Cl	50
$(NH_4)_2HC_6H_5O_7$(citrate)	65
NH_4OH (30%)	175 *ml./L.*
pH	9·0–9·2
Temperature (°C.)	25
Current density	
(amp./ft.²)	30
(amp./dm.²)	3·24

Deposits plated from this solution direct onto steel showed poor adhesion, but this defect was remedied by use of a preliminary cyanide-copper flash, permitting production of nickel coatings up to 25 mils. thick. The deposits were light grey and matte: with current densities above 30 amp./ft.² (3·24 amp./dm.²) the colour darkened, but with thin deposits no burning was observed with current densities up to 100 amp./ft.² (10·8 amp./dm.²). In such a solution the nickel ion supplies the source of metal, the ammonium ion provides a suitable complexing agent for the nickel, the chloride ion permits rapid anode dissolution, the citrate ion assists in complexing the nickel, and the hydroxide ion provides the selected pH value, maintenance of which is assisted by the citrate constituent. Cathode efficiencies with such a solution are too low to be satisfactory in commercial operation, but it is suggested that this limitation could easily be overcome by increasing the metal content.

It is urged that the information presented in this review indicates that production of nickel deposits from alkaline solutions has interesting possibilities. Further development work will be required, particularly with regard to reduction of stress in the deposits, which might be effected by use of organic addition agents.

Electrodeposition of Nickel-Molybdenum Alloys

D. P. ZOSIMOVICH and N. F. BOGATOVA: 'Use of Soluble Nickel-Molybdenum and Nickel Anodes for Electrodeposition of Nickel-Molybdenum Alloys from Alkaline Electrolytes.'

Zhur. Priklad. Khim., 1958, vol. 31, Mar., pp. 429–34.

Study of the behaviour of sintered nickel-molybdenum and nickel anodes in electrodeposition of nickel-molybdenum alloys from ammonia electrolytes and from alkaline ammonia/tartaric-acid solutions. It is shown that, over a wide range of current densities, it is possible to maintain the nickel concentration of the bath constant by etching the anodes and controlling the rate of their solution by variation in the Cl-ion concentration.

Electrodeposition of Nickel-Molybdenum and Nickel-Tungsten Alloys

T. F. FRANTSEVICH-ZABLUDOVSKAYA and A. I. ZAYATS: 'Electrodeposition of Alloys of Nickel with Molybdenum or Tungsten from Aqueous Ammonia Electrolytes.'

Zhur. Priklad. Khim., 1958, vol. 31, Feb., pp. 234–40.

The experiments reported indicated the possibility of electrodepositing both types of alloy from ammoniacal electrolytes containing no oxy acids. A study was made of the influence, on alloy composition, of composition of the solution, pH, temperature and current density.

Electrodeposition of Nickel-Zinc and Nickel-Molybdenum Alloys

S. K. PANIKKAR and T. L. R. CHAR: 'Electrodeposition of Nickel Alloys from the Pyrophosphate Bath: Nickel-Zinc and Nickel-Molybdenum Alloys.'

Jnl. Scientific and Industrial Research (India), 1958, vol. 17, Feb., pp. 95–6.

In continuation of work on the deposition of alloys of various types from pyrophosphate baths, the authors report successful experiments in production of the two types mentioned. A study was made of the effects, on the composition and properties of the deposited alloys, of variation in current density and metal content of the solutions.

In the nickel-zinc series adherent and dark-to-greyish white deposits containing 7–85 per cent. nickel were obtained by varying the operating conditions. The nickel content of the coatings increased with increase in the nickel content of the solution, with rise in temperature and with agitation. Addition of ammonium citrate (20 g./L.) considerably increased the percentage of nickel in the deposited alloy, whereas gelatin (1 g./L.) had the reverse effect.

Nickel-molybdenum alloys deposited from pyrophosphate solutions were grey to dark grey in colour.

Weathering Properties of Tin-Nickel-Alloy Electrodeposited Coatings

F. A. LOWENHEIM, W. W. SELLERS and F. X. CARLIN: 'The Protective Value of Tin-Nickel Alloy Deposits on Steel.'

Jnl. Electrochemical Soc., 1958, vol. 105, June, pp. 339–46.

Since the development, in 1951, by The Tin Research Institute, of a process for electrodeposition of tin-nickel alloys, various aspects of the subject have been closely studied. Papers published initially or in the intervening years have (1) shown that the deposit is an inter-metallic compound of the formula SnNi; (2) elucidated the function of the fluoride ion in complexing the tin in solution, (3) reported studies of the throwing power of the electrolyte, (4) dealt with the electrode potential of the alloy and

its resistance to many chemical reagents, (5) given data on the hardness of the alloy deposits, (6) proposed modifications in the composition of the solutions, and (7) reported results of outdoor weathering tests.

In view of the unusually interesting nature of the tin-nickel alloy deposits and of their obvious industrial usefulness, two important American companies have collaborated in an extensive test programme designed to supplement the information already obtained on atmospheric weathering properties. The basis metal used was cold-rolled mild steel, and the specimens exposed were prepared in such a way as to permit study of

(1) Effect of total thickness of coating (0·75–1·5 mils).

(2) Effect of type of undercoat used: the tin-nickel was deposited (1) direct on steel; (2) over a copper flash; (3) over substantial thicknesses of copper; or (4) over nickel.

(3) Effect of proportion of copper undercoating to final tin-nickel coating. (Copper undercoats of 0·25 to 1·0 mils were used.)

(4) Direct comparison of tin-nickel with nickel/chromium (thickness for thickness) over various thicknesses of copper. The nickel coating was in all cases deposited from a Watts solution and the coating was buffed before deposition of chromium.

(5) Effect of chromium over tin–nickel undercoat.

(6) Use of tin-nickel as a final flash coating, comparable with conventional chromium coatings. Copper or bronze undercoatings were used.

Comparisons and tests in all the series mentioned were made in two typical atmospheres: marine (Kure Beach corrosion-testing station) and industrial (Bayonne, N.J.).

Full details are given of plating conditions, exposure sites and placing of specimens, also methods of inspection and rating of behaviour. Tables and graphs report the ratings for individual specimens after the following periods:

Marine atmosphere: 7, 12 and 24 months.

Industrial „ : 6, 12, 24 and 29 months.

The relative merit of the various forms of coating differed appreciably under the two types of exposure. The results are therefore discussed separately. Among the main conclusions drawn are the following:

Marine-Atmosphere Exposure

All the panels deteriorated relatively rapidly: for long-time service in such atmospheres it would be necessary to use coatings thicker than those tested. Useful life of tin-nickel coatings was, in most cases, almost independent of the nature or thickness of the undercoat, but in order to obtain reasonably good performance a final tin-nickel coat of at least 1·0 mil appears to be required. In spite of early powdering-off of chromium from the chromium-plated tin-nickel coatings, the performance of such coatings was noticeably better than that of tin-nickel carrying no final coating of chromium. (This finding has been confirmed in other tests.) Tin-nickel plated direct on steel failed very rapidly, but even a thin flash of copper was sufficient to effect a 'dramatic' improvement. In comparing tin-nickel with nickel/chromium coatings, results for thinner coatings were not entirely consistent: in heavier coatings the two types appear to be roughly equivalent in performance.

Industrial-Atmosphere Exposure

The industrial atmosphere in which the exposures were made appeared to be of the same order of corrosiveness to nickel/chromium or copper/nickel/chromium coatings as the marine atmosphere at Kure Beach, but for the tin-nickel coatings the industrial atmosphere proved far less agressive than the marine conditions. Thus, at Bayonne the tin-nickel coatings consistently outperformed the nickel/chromium types. As in marine conditions, for a given thickness of coating, performance improved as the ratio of tin-nickel to copper undercoat increased. In this atmosphere also tin-nickel deposited direct on steel failed rapidly, but again even a thin undercoat of copper much improved the corrosion-resistance. There appears to be little to choose between nickel and copper as undercoats for tin-nickel: slight differences in comparable specimens favour copper.

Comments on Results Observed at Both Locations

(*a*) *Type of Failure.* When a nickel/chromium- and a tin-nickel-coated panel have failed to the same extent, as assessed by the rating scheme used, the two will probably not be similar in surface appearance. Nickel/chromium coatings normally fail by a multitude of small spots (pinhole rusting), of which more and more appear as deterioration proceeds: some of the spots may become enlarged and develop into craters or pustules of rust. Pinhole rusting is, however, a relatively rare defect in tin-nickel coatings, in which failure usually starts in a few spots which gradually grow in size. A typically low-rated tin-nickel panel may therefore have relatively few very large rust craters, and large areas of the panel may be entirely free from defects. (Typical differences are illustrated.)

(*b*) *Stain and Discolouration.* Tin-nickel coatings, which are initially of a more reddish hue than chromium, begin, after a relatively short period of exposure, to darken. The change is presumed to be due to formation of an oxide or some other type of film. Investigation of the possibility of protecting tin-nickel coatings by a conventional thin flash of chromium could not be successfully carried out due to flaking of the chromium. In a further series of tests, still under way, better results have been achieved in obtaining adherent chromium coatings, indicating some hope of utilizing a final coating of that type as tarnish-inhibitor. Study is also being made of the nature of the corrosion of tin-nickel coatings.

Electrodeposition of Tin-Nickel Alloys

K. M. TYUTINA and N. T. KUDRYAVTSEV: 'Electrodeposition of Tin-Nickel Alloy from Chloride-Fluoride Solutions.'

Zhur. Priklad. Khim., 1958, vol. 31, May, pp. 723–9.

A study was made of the electrodeposition of tin-nickel alloys from solutions of $NiCl_2$ and $SnCl_2$ containing additions of NaF and NH_4F. The composition of the deposit made from such solutions is tin 65, nickel 35, per cent.; it remains constant over a current-density range of 0·5–4 amp./dm.^{2} irrespective of the proportions of tin and nickel in the electrolyte. Addition of phenol sulphonic acid to the electrolyte was found to lower the tin content of the deposit to 50–53 per cent.

The authors report some results of corrosion tests made in various environments.

Non-Destructive Testing of Metallic Coatings

See abstract on p. 211.

Automatic Drag-Out-Recovery Plant

R. J. MALING: 'Efficient Drag-Out Recovery in Barrel Nickel Plating.'

Electroplating and Metal Finishing, 1958, vol. 11, June, pp. 184–9, 206.

The paper gives a detailed account of investigations which led up to the development, by the Bifurcated and Tubular Rivet Company, of an automatic system by which drag-out is recovered and continuously fed back to the plating bath.

The investigation had its source in the wide variation between the amount of inorganic salts estimated to be required to maintain the optimum concentration of the (organic-bright) solution and that which in practice was found to be needed.

Remedial efforts centred on two possible complementary procedures: economical rinsing of the barrels, and the use of the first rinse tank as a source of drag-out replacement. Change in volume of the solution was due almost entirely to evaporation, and after establishing the fact that the concentration required to replace loss by normal evaporation would be *less* than that obtainable in a triple counterflow rinse system, efforts were made to devise a continuous automatic method of effecting compensation for drag-out (without change in the volume of the plating solution) by use of the dilute solution contained in the rinse tanks.

Success depended on use of simple flow controls and, if the loss from the main bath was to be small, drag-out had to be related to the 'inefficiency' of the solution, i.e., the difference between the anode and cathode efficiencies. Control of temperature, pH and evaporation was also important. These factors are fully discussed in the paper, together with the calculations by which their importance was assessed.

The set-up in its final form incorporates a three-stage counterflow rinsing system for the line of ten barrels. As a barrel enters the system a prescribed volume of water is admitted to the third tank. Immersion of the barrel in the first rinse tank results in an overflow of a similar volume of drag-out, which eventually finds its way into a storage tank, whence it is fed at a controlled rate into the main plating bath. It is estimated that introduction of this system has resulted in an annual saving of £5,000; it also ensures greater control of the plating variables, and hence improvement in quality of the deposits.

NON-FERROUS ALLOYS

Cupro-Nickel Alloys: Properties, Fabrication and Applications

J. L. EVERHART: 'Cupro-Nickels Offer Corrosion-Resistance and Hot Strength.'

Materials in Design Engineering, 1958, vol. 47, May, pp. 114–20.

Reprint issued by INTERNATIONAL NICKEL CO., INC.

This review, which relates mainly to cupro-nickels of the 70–30 and 90–10 types, is divided into sections dealing with the mechanical properties of the alloys in wrought and cast form, and their corrosion-resistance, fabricating characteristics and applications.

Discussion of mechanical properties in the text is supplemented, in the case of the wrought alloys, by tabular data on physical and mechanical properties for annealed, half-hard and hard strip, and for annealed and light-drawn tubing. Typical properties for alloys in the cast form are also recorded. Reference is made to the beneficial effects of alloying with small amounts of iron, on resistance to corrosion by sea water, and brief consideration is given to the behaviour of copper-nickel alloys in acids, alkalis and other corrosives, low-temperature, creep and short-time high-temperature properties are also discussed.

Brief comment is made on cast alloys hardened by additions of carbon, silicon, manganese, aluminium and tin.

Fabrication characteristics of the 70–30, 80–20 and 90–10 cupro-nickels are discussed in relation to hot- and cold-working, casting, machining, and soldering, brazing and welding. Processing properties are summarized in a table.

Finally, a general review is presented of applications for which the respective cupro-nickels have proved suitable. Consideration of their major use, as materials for tubing in heat exchangers, condensers and evaporators, is supplemented by data on maximum allowable design stresses at various temperatures. Brief notes are also given on marine, food-processing, paper-making and coinage applications of the alloys.

F. W. NOTHING: 'Copper-Nickel Alloys containing less than 50 per cent. Nickel.'

Published by *Nickel-Informationsbüro G.m.b.H.*, Düsseldorf, 1958; 67 pp.

The publication gives a comprehensive survey (supplemented by a *bibliography* of 51 items) of the

properties, fabrication and applications of industrially important cupro-nickels. The scope of the contents is indicated below.

(1) *Structure and Classification of the Cupro-Nickels* (of simple and complex types).
(2) *Physical Properties*
(Colour, optical properties, thermal conductivity, thermal expansion, specific heat, electrical and magnetic characteristics.)
(3) *Mechanical Properties* (at normal, elevated and sub-zero temperatures).
(4) *Corrosion-Resistance.*
(General review of corrosion-resistance of the cupro-nickels, followed by information on resistance to atmospheric corrosion and to attack by acids, bases and salts, and by organic and gaseous materials.)
(5) *Working*
(Melting and casting; hot and cold working; heat-treatment; pickling; brazing and welding; machining.)
(6) *Properties and Applications of Industrial Alloys.*
(Binary alloys containing nickel up to 10, 15-30, and more than 30 per cent.; complex cupro-nickels containing, in varying combinations, tin, silicon, iron, manganese, aluminium, and other elements.)
(7) *Names and Compositions of Cupro-Nickels.*
(The list contains more than 100 trade names, used in various countries, for alloys which can be considered as basically cupro-nickels. The compositions of the respective types are broadly indicated.)
(8) *Applications*
(The applications are individually correlated with the description of the type(s) of cupro-nickels which may be used for the respective purposes.)
(9) *Tabular Data* supporting the text.

Constitutional Studies on Nickel-base High-Temperature Alloy Systems

See abstract on p. 227.

Nickel-Palladium-Manganese Alloys: Constitution and Properties

W. KÖSTER and M. SALLAM: 'The Ternary Nickel-Palladium-Manganese System.'

Zeitsch. f. Metallkunde, 1958, vol. 49, May, pp. 240-8.

Following an introductory section reviewing data on the related binary systems nickel-palladium, palladium-manganese and nickel-manganese, the authors report a detailed study of the ternary system, by metallographic methods, thermal analysis, and magnetic, dilatometric and X-ray examination. The report is profusely illustrated with photomicrographs of typical structures. Six alloys, containing 10 per cent. of manganese, with palladium 15, 30, 40, 50, 60 or 70, per cent., balance nickel, were studied with reference to the influence of thermal ageing treatments on hardness, electrical resistance, magnetic susceptibility, elastic modulus and coercive force

Magnetostriction Characteristics of Nickel-Copper and Nickel-Cobalt Alloys

M. YAMAMOTO and T. NAKAMICHI: 'Magnetostriction Constants of Nickel-Copper and Nickel-Cobalt Alloys.'

Jnl. Physical Soc. Japan, 1958, vol. 13, Feb., pp. 228-9.

Magnetostriction constants were determined, on single-crystal specimens, over the following concentration ranges:

Nickel-copper alloys up to 35 at. % copper.
Nickel-cobalt „ „ 55 wt. % cobalt.

The determinations were made at room temperature.

Thermal Properties of Alloys: Reference Data

See abstract on p. 211.

Creep of Nickel-Copper Alloys

See abstract on p. 231.

Resistance of 'Monel' and Cupro-Nickel to Hydrofluoric Acid

See abstract on p. 245.

Ageing/Magnetic-Properties Relations in Copper-Nickel-Iron Magnet Alloys

See abstract on p. 224.

Ageing Characteristics of Nickel-Chromium Alloys containing Aluminium and Titanium

See abstract on p. 227.

Age-Hardening Phenomena in Nickel-Chromium-base Alloys

See abstract on p. 228.

Coupling of Metallic Materials with Graphite: Effect on Corrosion-Resistance

See abstract on p. 245.

Nickel-containing Materials in Television Equipment

See abstract on p. 224.

Testing of Metallic Materials

See abstract on p. 211.

Analysis of Copper Alloys for Foundry Control

W. A. BURFORD: 'Simple Analytical Control for Small Foundries.'

Brit. Foundryman, 1958, vol. 51, June, pp. 280-2.

It is argued that since the composition limits of many specifications for copper alloys show fairly wide limits, adequate foundry control could be exercised by analytical methods less meticulous than those generally used. As a support to the proposal for simpler and more rapid methods, the author describes procedure for estimation, within practically useful limits of accuracy, of tin, lead, zinc, nickel and phosphorus in copper alloys.

The technique recommended is based on the use of a centrifuge to obtain the volumes of the various precipitates formed and conversion of these values into percentages by multiplying by suitable factors.

Analysis of Titanium Alloys

G. NORWITZ and M. CODELL: 'Composite Procedure for the Determination of Mo, Ni, Mn, Fe, Cr, Sn, V and N in Titanium Alloys.'

Metallurgia, 1958, vol. 57, May, pp. 261–70.

The methods described were developed as the result of research under a programme sponsored by Wright Air Development Center in the Pitman-Dunn Laboratories, Frankford Arsenal, Philadelphia, Pa., U.S.A. The procedure permits determination of several elements on aliquots taken from a master solution.

The method found optimum for dissolving the sample was by means of a mixture of moderately dilute sulphuric acid and a little hydrofluoric acid. The titanium was then oxidized with hydrogen peroxide and the solution was evaporated to fumes of sulphuric acid. In this treatment the silicon is volatilized as silicon tetrafluoride and the boron as boron trifluoride. Up to 4 per cent. of tungsten can be held in solution, due to the solvent action of titanium on tungstic acid. If more than this amount of tungsten is present, the small amount of precipitate which remains can easily be filtered off.

After determination of the optimum master solution, procedures were devised for estimation of the respective elements. Full details are given of methods for estimation of *molybdenum* (colorimetrically with thiocyanate, or gravimetrically or volumetrically after a sulphide precipitation); *nickel* (colorimetrically or gravimetrically with dimethylglyoxime); *manganese* (by the periodate colorimetric method, or by titration with arsenite); *iron* (colorimetrically with orthophenanthroline or by titration with dichromate); *chromium* (colorimetrically with diphenylcarbazide or by titration with ferrous sulphate); *tin* (iodometrically); *vanadium* (by titration with ferrous sulphate, using sodium diphenylbenzidine sulphonate indicator); *nitrogen* (volumetrically, after distillation). The limits of applicability for estimation of each element are indicated.

Welding of Cupro-Nickel and Aluminium-Bronze Alloys

C. A. TERRY and E. A. TAYLOR: 'Welding of Cupro-Nickel and Aluminium-Bronze Alloys.'

Brit. Welding Jnl., 1958, vol. 5, May, pp. 211–25.

The corrosion-resistance of the aluminium bronzes and cupro-nickel alloys has long been successfully utilized and the alloys are now finding extending application, particularly in the marine and chemical-engineering fields. In such cases fabrication of components is frequently effected by welding. The authors of the present paper critically discuss methods suitable for these materials.

Cupro-Nickel Alloys

The review covers the use of argon-arc, inert-gas metallic-arc, metallic-arc, and gas techniques of welding. Factors affecting weldability are discussed, with particular reference to the deleterious influence of trace impurities and to methods for avoiding gas porosity in the welds. In each case recommendations are made with respect to preparation of the joints and welding procedure. Tabular summaries are made of mechanical properties typical of welds produced by the respective processes in 94–5–1 copper-nickel-iron alloys and in 80–20 and 70–30 copper-nickel alloys. Some of the main points of the discussion are briefly noted below.

In connexion with inert-gas shielded-arc welding processes, attention is directed to improved filler alloys which have been developed to overcome porosity: advantages so gained are demonstrated by a table showing properties typical of welds made with the new filler materials.

In preparation of joints and selection of welding technique, thickness of the material is significant: recommendations are made as to preferred procedure.

For metallic-arc welding of cupro-nickel alloys use has been made of electrodes having core wires of 'Monel' containing addition elements incorporated to prevent porosity and other undesirable features. Such electrodes are not, however, ideal for the purpose and recently a special type of 70–30 cupro-nickel electrode has been introduced. It has also been shown that filler materials which have proved suitable for inert-gas metal-arc welding may usefully be employed also as the core material for coated electrodes. Such electrodes are stated to be in course of development.

Due to risk of gas porosity, autogenous gas welding of binary copper-nickel alloys has until now been restricted to joining of thin sheet up to only about $\frac{1}{16}$-in. (0·15-cm.) thick, but recent work on cupro-nickel filler rods containing powerful deoxidants indicates that the range of thickness which can be handled by this method may be somewhat extended in the future.

Aluminium Bronzes

The format of the second part of the paper is closely similar to that of the section dealing with cupro-nickel alloys. General information is given on the aluminium bronzes which are of industrial importance, and reference is made to factors affecting their weldability (e.g., the presence of tenacious oxide films). The relevant portions of the copper-aluminium, copper-aluminium-iron and copper-aluminium-nickel systems are briefly discussed in relation to cracking in the welds, and the conditions pre-requisite to satisfactory welding by the metallic-arc and other processes are reviewed. Attention is directed, *inter alia*, to the findings of the British Non-Ferrous Metals Research Association on the harmful effects of traces of lead and bismuth in filler wires and the corrective effect of lithium additions.

The major portion of this section of the paper deals, however, with the inert-gas shielded-arc welding

of an aluminium-bronze to A.S.T.M. Specification B 171 *Type D* (copper 88–92, aluminium 6–8, iron 1·5–3·5, per cent.). Despite assertions in the literature that sound welds are consistently achieved in aluminium bronzes by this technique, cracking and brittleness have been reported in the underbeads of multi-run welds. To investigate the susceptibility of aluminium-bronze alloys to weld cracking and weld brittleness, tests were carried out by the authors, using five filler materials; two of these (A.S.T.M. alloy *E* and 'Superston') were nickel-aluminium bronzes, another was alloy *D*, and the remainder aluminium bronzes of the 93–7 type. Full details are given of the testing procedures used, and the results, which are supplemented by photomicrographs of the various weld metals, are discussed in relation to theories previously advanced to account for weld cracking and weld brittleness.

Hot-cracking susceptibility was found not to be a serious problem: alloy *D* was slightly more susceptible than alloy *E* and slightly less susceptible than 'Superston'. Intercrystalline cracks did, however, occur in the 93–7 weldment. Addition of small amounts of lithium to alloys *D* and *E* and to 'Superston' increased resistance to cracking: this effect is interpreted in terms of sub-solidus hot-shortness. Root embrittlement occurred in a seven-pass weld.

From the point of view of strength, the most satisfactory filler was alloy *E* (copper 81·26, aluminium 9·14, nickel 5·12, iron 2·83, manganese 1·33, zinc 0·23, lead < 0·01, bismuth < 0·001, per cent.), since it so overmatched the properties of the basis metal that failure always occurred away from the weld. It is emphasized, however, that in certain media alloy *E* is less corrosion-resistant than alloy *D*.

The authors summarize their conclusions as follows: 'It is evident that the hot-cracking susceptibility of aluminium-bronze alloys is small and, with correct welding procedure, is unlikely to cause trouble in practice. The conditions under which weld-root embrittlement occurs have not been defined; certainly it does not invariably occur and the evidence suggests it is related to minor impurities rather than brittle grain-boundary films of gamma. The problem could be studied . . . either by using high-purity materials or possibly by adding small quantities of lithium to filler rods.'

NICKEL-IRON ALLOYS

Properties of Simple and Complex Nickel-Aluminium-Iron-base Magnet Alloys

A. A. SHEKALOV and Y. I. SHTREIS: 'Investigation of the Mechanical and Magnetic Properties of Fe-Ni-Al Alloys for Permanent Magnets.'

Metallovedenie i Obrabotka Metallov, 1958, No. 4, Apr., pp. 29–38.

Report of a systematic study of the properties of nickel-aluminium-iron and nickel-aluminium-copper-iron alloys containing iron 50–90, nickel 5–30, per cent. The work included determination of the influence, on mechanical and magnetic properties, of additions of various other alloy elements, including sulphur, titanium and lithium.

Ageing/Magnetic-Properties Relations in Copper-Nickel-Iron Magnet Alloys

V. I. IVANOVSKII: 'Magnetic Properties of Fe-Mo and Cu-Ni-Fe Alloys during Ageing.'

Fizika Metalov i Metallovedenie, 1957, vol. 4, pp. 245–8.

Study of variations in magnetic properties, during ageing, of iron-molybdenum alloys (18% Mo) and copper-nickel-iron alloys (Cu 52, Ni 36, Fe 12, at. %).

Nickel-containing Materials in Television Equipment

'New for Television. A Short Cathode-Ray Tube for Monochrome and Colour.'

Engineering, 1958, vol. 185, May 16, pp. 620–3.

In conventional cathode-ray tubes the beam approaches the screen in a straight line, like a pencil pivoted at its end. In the new flat form of tube described in this article the beam is folded over on itself, and runs for most of its length parallel to the picture screen, bending towards it only on the last short section of its trajectory. Although more expensive in itself than a conventional tube, some economies in circuit design and cabinet construction can be gained by use of the new model, and the technical advantages in the electron optics and the automatic self-scanning system involved render it an outstanding advance on earlier designs. A particular feature is the simplicity with which the new tube can be used for colour reproduction: it thus offers the combination of two steps in one, from monochrome to colour and from cods-eye to flat screen, which can be hung on a wall. Design and operation are described, with detailed illustration, in this excerpt from a paper recently presented by D. GABOR, P. R. STUART and P. G. KALMAN before the Institution of Electrical Engineers. The development is the outcome of research at the Imperial College of Science and Technology, in association with the National Research Development Corporation.

It is noted that several nickel-containing alloys having specialized physical properties are variously utilized in the new tube, e.g., 'Permalloy' (soft-magnetic nickel-iron alloy), 44–56 per cent. nickel-copper non-magnetic alloy, and nickel-chromium alloy.

CAST IRON

Enamelling of Spheroidal-Graphite and Other Cast Irons

D. KAMRAN: 'Study of Processes Occurring during Enamelling of Cast Irons.'

Giesserei, 1957, vol. 44, Nov. 21, pp. 705–13.

The paper reports a study planned to secure inform-

ation on the factors which govern the enamelling characteristics of cast iron.

Data are presented on the oxidation-resistance of cast-iron specimens with and without coatings of enamel, and details are given of experiments on cast iron and steel plate which had been polished and shot-peened prior to enamelling, to determine the effect of surface finish on adherence of the enamel. Finally, the author reviews the results of a study of the influence of composition, superheating and re-melting, on adherence.

Previous work had shown that excellent adhesion was obtainable in enamel coatings applied to ferritic cast iron in which the flake graphite was finely dispersed throughout the matrix. On the assumption that even better results would be achieved by use of annealed S.G. iron, further experiments were carried out. The data obtained confirmed the superiority of spheroidal-graphite iron, demonstrating that adhesion of the enamel on this material was better than that obtained with any other type of cast iron.

CONSTRUCTIONAL STEELS

Volume Change of Steel at Ac_3 Temperature: Effect of Alloying Elements

A. S. KENNEFORD: 'The Effect of Some Common Alloying Elements on the Volume Change at Ac_3 of a 0·35% Carbon Steel.'

Jnl. Iron and Steel Inst., 1958, vol. 189, June, pp. 135–8.

The effect of various alloying elements on the volume change during the $\alpha \rightarrow \gamma$ transformation was studied dilatometrically, in a series of alloy steels containing 0·35 per cent. carbon. Rate of heating and cooling was 5°C./min., with a maximum temperature of about 1000°C.

Eight series of steels were examined:

		%	
(1)	Carbon steels containing	0·3–1	Carbon
(2)	Steels containing silicon	0·5–3	Carbon in all cases about 0·35%
(3)	„ „ manganese	0·5–2·5	
(4)	„ „ nickel	0·5–5	
(5)	„ „ chromium	0·5–3	
(6)	„ „ molybdenum	0·25–1	
(7)	„ „ vanadium	0·05–0·3	
(8)	„ „ cobalt	0·5–4	

Of the elements investigated, silicon and molybdenum were found to decrease volume change: manganese, nickel, chromium and cobalt had the reverse effect. Under the test conditions employed, small amounts of vanadium resulted in a slight increase in volume change, but vanadium in excess of 0·05 per cent. caused a slight progressive lowering in contraction at transformation. It is possible that with slower rates of heating and cooling and a higher maximum temperature different results would be obtained with this element.

Ferrite-soluble elements (silicon, manganese, nickel and cobalt), which might have been expected to behave similarly to each other but differently from those with strong carbide-forming tendencies (chromium, molybdenum and vanadium), did not show the results anticipated: nor was similar behaviour observed in elements, which, according to their various equilibrium diagrams with iron, show similar characteristics. The silicon-iron, molybdenum-iron and chromium-iron systems all, for example, exhibit a closed γ-loop, but whereas silicon greatly reduces the contraction in volume, molybdenum has only a slightly reducing effect, and chromium has a strongly increasing effect.

Thermal Properties of Steels: Reference Data

See abstract on p. 211.

Elevated-Temperature Properties of Welds in Steels and Alloys

See abstract on p. 239.

Design Properties of High-Strength Low-Alloy Steels

B. B. MUVDI, G. SACHS and E. P. KLIER: 'Design Properties of High-Strength Steels in the Presence of Stress Concentrations (and Hydrogen Embrittlement).' *Wright Air Development Center, Tech. Report* 56-395, *Parts I–III*, Dec. 1956.

Efforts to develop materials possessing the high strength-to-weight ratios required to meet the demands of the aircraft industry have entailed extensive testing of low-alloy steels heat-treated to strengths in the range 200,000–300,000 p.s.i. (90–133 t.s.i.; 140–210 kg./mm.²). Previous investigations had demonstrated that steels at that level are subject to design criteria which vary in many respects from those applicable at lower strengths. The three parts of this report (see abstracts below) present the results of a series of investigations to determine the properties of typical high-strength steels. All are variants derived from the basis S.A.E. 4340 nickel-chromium-molybdenum type*: the modifications are concerned mainly with the manganese and silicon contents.

Part I: 'Dependence of Tension and Notch-Tension Properties of High-Strength Steels on a Number of Factors'; 57 pp. *PB* 121847.

This report deals with the static-tension properties of smooth and notched specimens of the following types of steel: S.A.E. 4340, V-Mod. 4330, 98B40, 'Tricent', 'Hy-Tuf', 'Super Hy-Tuf' and 'Super TM-2'. The tests were designed to evaluate the influence of the following variables: composition, direction of testing, section-size, sharpness of notch or stress concentration, and strength level or tempering temperature. The strengths of the steels tested lay in most cases within the limits 180,000–300,000 p.s.i. (80–133 t.s.i.; 126–210 kg./mm.²).

Tensile strength was, in general, found to be independent of the orientation of the specimen, and

* S.A.E. 4340. Carbon 0·38-0·43, silicon 0·20-0·35, manganese 0·60-0·80, nickel 1·65-2·00, chromium 0·70-0·90, molybdenum 0·20-0·30, per cent.

decreased gradually with increase in the specimen size. The ductility of smooth specimens was, however, influenced by both orientation and size of specimen.

Notch strength decreased with increase in stress concentration, diameter of specimen, section-size and change in orientation of the specimen from longitudinal to transverse. These effects, pronounced at high levels of strength, decreased with fall in tensile strength, until at values below 200,000 p.s.i. (90 t.s.i.; 140 kg./mm.^{2}) they became insignificant. Where individual steels deviated from these general qualitative trends, this fact is indicated and their behaviour is discussed.

Part II: 'Axial-Load Fatigue Properties of High-Strength Steels'; 38 pp. *PB* 121883.

The paper has also been published in *Proc. Amer. Soc. Testing Materials*, 1957, vol. 57, pp. 655-66.

Axial-load fatigue tests were made on notched and unnotched specimens of 'Tricent', 'Crucible SHS-260' and 'Super TM-2' steels, to evaluate the effect, on fatigue properties, of stress concentration, strength level (250,000-300,000 p.s.i.; 111-133 t.s.i.; 175-210 kg./mm.^{2}), and orientation of specimen.

Fatigue strength was found to decrease with increase in stress concentration, reaching a minimum for stress-concentration factors between 1 and 3. Endurance limit appeared to be determined by the tensile strength of the steel: a minimum value was found at a U.T.S. of 240,000-260,000 p.s.i. (107-116 t.s.i.; 168-183 kg./mm.^{2}), with increase to a maximum at a tensile strength in the range 270,000-300,000 p.s.i. (120-133 t.s.i.; 190-210 kg./mm.^{2}). Endurance limit was, in general, lower for transverse than for longitudinal specimens, and the effects of specimen orientation were more pronounced in un-notched specimens and at high levels of strength.

Part III: 'The Response of High-Strength Steels in the Range of 180,000-300,000 p.s.i. to Hydrogen Embrittlement from Cadmium Electroplating,† 116 pp. *PB* 131034.

For abstract of this paper see *Nickel Bulletin*, 1958, vol. 31, No. 1, pp. 12-13.

Brittle Fracture Studies on Nickel Steel

G. M. ORNER: 'Charpy Brittle-Fracture Transitions by the Lateral Expansion-Energy Relationship.'

Welding Jnl., 1958, vol. 37, May, pp. 201s-5s.

Precise determination of transition temperature has been the subject of considerable controversy and there is as yet no universally accepted criterion for determination of the temperature at which fracture behaviour changes from tough to brittle. Recent investigations at Watertown Arsenal have indicated that, by a variation of the conventional Charpy impact-testing technique, transition temperature may be determined on the basis of a concept that a brittle crack is propagated by the continuous release of the elastic-stress field in the material surrounding the crack. This procedure, which distinguishes between the crack-initiation and crack-propagation stages, requires initiation of a crack by means of a low-energy blow, and propagation effected by a full-capacity blow of the impact-machine pendulum. The authors have proposed a definition of transition temperature which they consider to be of fundamental significance, *viz.*, the maximum temperature at which a self-propagating crack can initiate in a cross section of infinite dimensions. In this paper it is shown that in the plot of energy-to-fracture *vs.* lateral expansion there is a discontinuity which corresponds quantitatively with the low-blow transition temperature, thus providing further evidence of the fundamental nature of the low-blow transition. Certain anomalous effects observed are attributed to adiabatic temperature rise which, in conventional (single-blow) impact testing, can produce fictitiously low transition curves, particularly in sub-size or keyhole Charpy impact specimens.

The work reported in this paper was carried out on normalized pearlitic steel of the following composition: carbon 0·14, silicon 0·23, manganese 0·50, sulphur 0·04, nickel 3·30, per cent. The microstructure of the steel and its typical energy-temperature transition curve, as determined by conventional methods, are correlated with the data obtained by the low-blow technique.

Low-Alloy-Steel Tubes and Fittings

AMER. SOC. TESTING MATERIALS: 'Proposed Tentative Specifications for Seamless and Electric-Welded Low-Alloy Steel Tubes for Economizers.'

Contained in Report of A.S.T.M. Committee A-1 on Steel.

A.S.T.M. Preprint 1, June 1958, pp. 25-31.

Tubes of the grade covered are for service under pressure in applications in which corrosion-resistance is of importance. Properties, tests and dimensional requirements are laid down. Chemical-composition limits (%): carbon 0·15 max., silicon 0·10 min., manganese 0·55, sulphur 0·06 max., phosphorus 0·06-0·16, chromium 0·24-1·31, nickel 0·20-0·70, copper 0·20-0·60.

'Proposed Tentative Specifications for Factory-Made Wrought Carbon Steel and Alloy Steel Welding Fittings of Seamless or Welded Construction for Low-Temperature Service', *ibid.*, pp. 49-57.

Relates to fittings for use in pressure piping and pressure vessels for service at low temperatures. The steels specified as suitable are the following types, to given A.S.T.M. specifications: carbon; 3½ per cent. nickel; 5 per cent. nickel; low-alloy chromium-copper-nickel-aluminium steel. Properties and methods of manufacture, heat-treatment and testing are stipulated, and emphasis is placed on impact properties in relation to temperature.

Testing of Metals

See abstract on p. 211.

† The information contained in this paper is closely related to that given in a paper, of the same title and by the same authors, published as *Amer. Soc. Testing Materials, Preprint* 78, June 1958; 23 pp.

HEAT- AND CORROSION-RESISTING MATERIALS

Constitutional Studies on Nickel-base High-Temperature-Alloy Systems

I. I. KORNILOV and R. S. MINTS: 'Investigation of the System Ni-Cr-NiAl.'

Zhur. Neorg. Khim., 1958, vol. 3, Mar., pp. 699-707.

Ternary phase diagram of the system Ni-Cr-NiAl, with supporting data on the systems Ni-NiAl and Cr-NiAl. Among the data reported are the hardness, electrical conductivity and its temperature coefficient, and the coefficient of thermal expansion of various alloys within the Ni-Cr-NiAl system.

P. B. BUDBERG: 'Investigation of Alloys in the Ternary System Nickel-Aluminium-Tungsten.'

ibid., 1958, vol. 3, Mar., pp. 694-8.

The alloys studied contained up to 30 per cent. aluminium and up to 60 per cent. tungsten. The paper includes isothermal sections of the ternary diagram at 800°, 1000° and 1200°C.

I. I. KORNILOV and E. N. PYLAEVA: 'The Binary Systems Ni_3Ti-Ni_3Ta and Ni_3Ti-Ni_3Nb.'

ibid., 1958, vol. 3, Mar., pp. 637-77.

The paper is well illustrated by diagrams, photomicrographs and tables of properties covering the complete range of the systems studied.

A. P. SMIRYAGIN, A. Y. POTEMKIN and R. P. MARTYNYUK: 'The Nickel - Molybdenum - Chromium Phase Diagram.'

ibid., 1958, vol. 3, Apr., pp. 853-9.

Report on investigation of the nickel-rich corner of the ternary diagram, covering compositions up to 40 per cent. molybdenum and 40 per cent. chromium. (Claimed to be the first study of this section of the diagram.)

Ageing Characteristics of Nickel-Chromium Alloys containing Aluminium and Titanium

N. E. ROGEN and N. J. GRANT: 'Ageing Characteristics of Nickel-Chromium Alloys containing Appreciable Amounts of Titanium and Aluminium.'

Amer. Soc. Testing Materials, Preprint 82, June 1958; 12 pp.

Researches in various countries have confirmed that age-hardening in the important alloy group based on Ni-Cr-Al-Ti is dependent on the precipitation and distribution of intermetallic phases and carbides and nitrides, and it has been shown that the titanium/aluminium ratio has an important effect on the mechanical properties obtainable at elevated temperatures. The present paper opens with a review of some of the major literature relevant to the constitution of this group of alloys and of the more complex cobalt-containing and other types which have been developed from the original quaternary base.

The aim of the experimental work described was extension of the study of the ageing characteristics and mechanical properties of simple Ni-Cr-Al-Ti alloys containing Ti+Al in excess of 4 wt. per cent. In the alloys studied the total content of the two elements varied from 4 to 6 wt. per cent. (6·4 to 8·8 at. per cent.) and the Ti/Al ratio ranged from 1·0 to 1·6: see table, p. 228.

Electrolytically extracted precipitates were examined and measurements were made of particle size and lattice-parameter. Variation of hardness was studied as a function of temperature and time of ageing (see details of thermal treatment below) and in relation to particle size of the precipitated phase. Stress-rupture properties were determined at 1500°F. (815°C.) and were correlated with the ageing characteristics observed.

Processing of Test Materials

All the alloys were received as forged-bar stock of $2\frac{1}{4}$-in. (58-mm.) diameter, made from vacuum-melted and -cast material. The bars were re-forged to $\frac{3}{8}$-in. diameter. Alloys 8v, 10v and 11v (see table, p. 228) were easily forged to the $\frac{3}{8}$-in. (10-mm.) diameter size: 13v forged only with considerable difficulty to $\frac{1}{2}$-in. (12-mm.) diameter, and 12v cracked during forging. The forging temperature was 2200°F. (1204°C.) and was not allowed to fall below 1900°F. (1038°C.). Six different heat-treatments were used for each alloy:

(1) Solution treated 5 hrs. at 1900°F. (1038°C.); oil-quenched; aged 24 hrs. at 1400°F. (760°C.).

(2) Solution treated 5 hrs. at 1900°F. (1038°C.); oil-quenched; aged 2 hrs. at 1600°F. (870°C.).

(3) Solution treated 4 hrs. at 2000°F. (1093°C.); water-quenched; aged 24 hrs. at 1400°F. (760°C.).

(4) Solution treated 4 hrs. at 2000°F. (1093°C.); water-quenched; aged 2 hrs. at 1600°F. (870°C.).

(5) Solution treated 2 hrs. at 2250°F. (1232°C.); water-quenched; aged 24 hrs. at 1400°F. (760°C.).

(6) Solution treated 2 hrs. at 2250°F. (1232°C.); water-quenched; aged 2 hrs. at 1600°F. (870°C.); (Too brittle to test).

Solution and ageing temperatures were selected to produce significant variations in structure, in order to facilitate correlation of structure and strength properties.

Among the conclusions drawn, which are discussed at some length, are the following:

'The lattice parameter of the ordered face-centred-cubic $Ni_3(Ti,Al)$ is affected by many factors, among which are ageing temperature and time, chemical composition, metallic radii and lattice positions, and the diffusion rates of titanium and aluminium. (Titanium diffuses at a slower rate than aluminium.) Because of these many contributing factors, it is most difficult to explain the parameter value resulting from the non-equilibrium conditions of heat-treatment.' (The degree of misfit between matrix and precipitate, and the hardness of some of the alloys examined, are recorded.)

Compositions of Alloys Studied

Composition (wt. %)							
Alloy	Chromium	Titanium	Aluminium	Carbon	Manganese	Silicon	Nickel*
8v.	20·71	2·98	1·43	0·04	—	—	74·79
10v.	19·30	3·07	2·09	0·03	0·05	0·004	75·46
11v.	19·78	3·85	1·38	0·03	—	—	74·91
12v.	18·89	2·89	3·12	0·04	—	—	75·01
13v.	18·90	3·97	2·05	0·03	—	—	75·00

Composition (at. %)							
Alloy	Chromium	Titanium	Aluminium	Carbon	Nickel	Titanium + Aluminium	Titanium/ Aluminium Ratio
8v.	22·06	3·47	2·95	0·18	71·06	6·42	1·18
11v.	21·11	4·46	2·84	0·14	70·86	7·30	1·57
13v.	20·15	4·59	4·21	0·14	70·85	8·80	1·09

* Nickel content by difference.

'In the nickel-chromium-titanium-aluminium system the following variables have an important effect on the particle size of the $Ni_3(Ti,Al)$ precipitate: solution treatment, ageing time and temperature, aluminium + titanium content and Al/Ti ratio, composition of the matrix.' (The effects of these variables are illustrated.)

'Electrolytic extraction was found to be an effective technique for the near-quantitative separation of the precipitate from the matrix. By use of this method the amount of precipitating phase can be determined gravimetrically and particle size may be measured by X-ray technique.

'Attempts to correlate particle size, spacing, and rupture strength at 1500°F. (815°C.) failed to establish any consistent relationship. It is probable that other factors, such as grain-size and stability of the precipitate, must also be taken into consideration.

'In the higher aluminium + titanium alloys which were examined in this investigation high-temperature strength was found to increase with increasing content of solute, but was much less affected by variations in the titanium/aluminium ratio beyond about 1·1 to 1.'

See also

Age-Hardening Phenomena in Nickel-Chromium-base Alloys

N. E. ROGEN and N. J. GRANT: 'Further Evidence of Zoning in a Nickel-Chromium-Titanium-Aluminium Alloy.'

Trans. Metallurgical Soc., Amer. Inst. Mining and Metallurgical Engineers, 1958, vol. 212, Apr., pp. 218–19; *T.N.* 463*E*.

Age-hardening in nickel-chromium-titanium-aluminium alloys in the composition range covered by the 'Nimonic' group of alloys is dependent on precipitation of the $Ni_3(Al,Ti)$ (γ') phase, which precipitates at about 700°C.

It has been suggested that some re-arrangement of structure (zoning) occurs in the supersaturated solid solution prior to actual precipitation of the hardening phase. The work reported here provides further demonstration of this change. It appears likely that the magnitude of the preliminary structural change is dependent, to a significant extent, on the aluminium and titanium contents of the alloy.

Ageing of 'Hastelloy B': Effect on High-Temperature Ductility

R. E. CLAUSING, P. PATRIARCA and W. D. MANLY: 'Ageing Characteristics of 'Hastelloy B'.

Trans. Amer. Soc. Metals, 1957, vol. 51, *Preprint* 79; 9 pp.

Nickel-molybdenum-base alloys of the 'Hastelloy B' and 'Hastelloy C' types have, for some years past,

been finding increasing application in many branches of the chemical industry, and some of their properties make them attractive for use in components of nuclear reactors. It has been observed, however, that in the range 1200°–1400°F. (650°–760°C.) 'Hastelloy B' shows low ductility: the incidence of cracking of the base metal in the heat-affected zone of welds, under conditions of severe restraint, has been attributed to this characteristic. As a preliminary to investigation from the point of view of welding, it was considered desirable to study ductility *per se*, in relation to structural effects occurring on prolonged exposure to elevated temperatures.

The material used was 'Hastelloy B' sheet, 0·065 in. (0·162 cm.) thick, having the composition molybdenum 27·0, iron 5·5, chromium 0·6, silicon 0·6, carbon 0·035, per cent., nickel balance. Tensile tests were made both at room temperature and at various elevated temperatures, using, in all cases, a strain rate of 0·05 in./0·12 cm. The tensile specimen is illustrated. Both solution and ageing treatments were carried out under 'bright heat-treatment' conditions. Preliminary solution treatment was in the range 2100°–2150°F. (1150°–1175°C.), and ageing was for 100, 500 and 1000 hours at 1100°, 1300°, 1500° and 1600°F. (593°, 720°, 815° and 870°C.). Tables show room-temperature and elevated-temperature tensile strength and ductility (per cent. elongation), as affected by the respective treatments, and photomicrographs correlate structural changes with the tabular data. (In the room-temperature tests hardness values are also reported.)

The following observations are made:

At 1300°F. (720°C.) this type of alloy shows rapid precipitation of a Widmanstätten-type structure, which is tentatively identified as the β phase of the nickel-molybdenum binary diagram. After ageing at 1100°F. (593°C.) for periods up to 1000 hours it was not possible, by either conventional or electron microscopy, to resolve the β constituent, but changes in hardness and mechanical properties indicated its presence.

The precipitate formed on ageing at temperatures of 1500°F. (815°C.) and above differed from that observed at lower temperatures, in that it was acicular rather than Widmanstätten in type. By analogy with the nickel-molybdenum diagram, it is suggested that this is the γ phase.

Ageing produces relatively minor improvements in room- and elevated-temperature tensile strength, but this is associated, in all cases, with marked reduction in ductility. The most serious drop occurred on ageing at 1300°F. (720°C.) and was associated with the presence of the Widmanstätten-type precipitate. Significant loss in ductility, accompanied by rise in room-temperature hardness, results from ageing at 1100°F. (593°C.): this change appears to be caused by formation of a submicroscopic β precipitate.

High-Temperature Properties of Nickel/Al_2O_3 Compositions

W. S. CREMENS and N. J. GRANT: 'Preparation and High-Temperature Properties of Nickel-Al_2O_3 Alloys.' *Amer. Soc. Testing Materials, Preprint* 83, June 1958; 17 pp.

Work on dispersion-hardened materials of the SAP type has indicated that attainment of optimum creep-rupture properties and high-temperature stability is determined to a great extent by the following factors: (1) use of an average inter-particle spacing of less than 1μ; (2) use, as the dispersion-hardening constituent, of a stable refractory particle with minimum solubility in the matrix material; and (3) extrusion of the compact, after sintering, to ensure a high rate of deformation and storage of energy in the structure. On the basis of these criteria, it was decided to investigate the high-temperature properties of nickel hardened with a fine dispersion of alumina. The choice of nickel as the metal constituent was dictated by consideration of its high melting point and good oxidation-resistance and because it is available in particle sizes of 1-2μ. Al_2O_3 was chosen on account of its high-temperature stability, high melting point and availability in particle sizes down to 0·02μ. The Al_2O_3 content of the materials tested was varied up to 45 vol. per cent.

Mixing, compacting, sintering and extrusion procedures used to produce the materials are discussed, as affecting the quality of the compacted material.

Mechanical properties were determined at room temperature, and elevated-temperature stress-rupture characteristics were investigated. Most of the latter determinations were made at 1500°F. (815°C.), considered to be the highest temperature compatible with the oxidation-resistance of nickel, but some specimens of both nickel and nickel-Al_2O_3 were subjected to tests, at 1300° and 1800°F. (705° and 980°C.), to evaluate the effects of temperature. The results are correlated with similar data for pure sintered nickel, 'A' nickel, 'Duranickel' and 'Inconel'.

It was found that the ideal distribution of oxide in fine metallic powders typical of the SAP-type product was not an essential pre-requisite to improvement in high-temperature properties in the nickel-alumina material, though the importance of inter-particle spacing with respect to creep-resistance was confirmed. The relation between stress-for-rupture in a fixed time and the reciprocal of the inter-particle spacing was found to be approximately linear. (A topological relationship is advanced to relate average inter-particle spacing in the matrix to the proportion and particle size of the dispersed phase.)

Stress-rupture properties of the strongest extruded 'alloys' were comparable with those of some conventional alloys, and room-temperature ductility of compositions containing less than 10 vol. per cent. of alumina was high. For all the materials elongation at 1500°F. (815°C.) was generally in the range of 2-4 per cent. The influence of the oxide constituent on room-temperature strength of nickel

was slight, by comparison with the very pronounced effect exerted at elevated temperatures.

The results are considered by the authors to offer promise that, by means of finer dispersions of alumina in the nickel matrix, it may be possible to obtain even higher rupture strengths, on a par with those of the heat-resisting alloys.

Impact-Resistance of Cermets: Effect of Metallic Surface Coatings

A. C. PEZZI and H. P. KLING: 'Improvement of the Impact-Resistance of Cermets.'

Wright Air Development Center Tech. Report 56-329, Apr. 1957; 27 pp.

Relatively disappointing results have been obtained in the many attempts which have been made to increase the bulk ductility and impact-resistance of cermet materials which, in some other respects, hold promise for use in gas-turbine blading. The authors of this report based their investigation on the assumption that impact failures in such materials originated in brittle cracks which form on the surface of the composite under tensile stress, and that therefore greater toughness, resulting in lessened susceptibility to brittle failures, might be achieved by formation, on the cermet surface, of an integral coating more metallic in nature than the bulk mass of the cermet. The line of approach thus differed fundamentally from earlier efforts, which have centred on modification of the composition of the total mass, or on change in fabrication methods. The specification requirement laid down was production of a specimen $\frac{3}{16}$ in.× $\frac{3}{16}$ in.× $1\frac{1}{2}$ in. (0·45 cm.× 0·45 cm.× 3·5 cm.), the impact-resistance of which, in the range room temperature to 1800°F. (980°C.), would be at least 20 in.-lb.

The cermet selected for the investigation was of titanium-carbide base, containing 20 per cent. of metallic binder (nickel 17, molybdenum 3, per cent.) and 6 per cent. of a complex (Nb-Ta-Ti) carbide. (This cermet has been developed under the designation 'K 161 B' and its properties are already known.) The materials used for the coatings, and methods by which they were applied, are indicated below.

(1) *High-Temperature Brazes*

The powder alloys used were bonded, applied to the surface of the cermet, and fired so as to fuse the braze alloy and drive off the binder material. Attempts to obtain satisfactory coatings with various nickel-base brazing alloys and nickel and copper powders, by firing in a hydrogen atmosphere, were unsuccessful, but blister-free coatings were obtained by brazing *in vacuo*. 'Nicrobraz' and a 50-50 nickel-chromium alloy thus deposited were evaluated as coatings.

(2) *Diffusion-Bonded Nickel Electrodeposited Coatings*

Blister-free coatings were obtained by electrodeposition of 0·0001 in. (0·0025 mm.) of nickel, firing *in vacuo* to bond the deposit, electrodeposition of a further 0·002-in. (0·05 mm.) deposit, and final firing at 1830°F. (995°C.).

(3) *Infiltrated 'Nichrome V' Coatings*

The cermet surface was diffusion-bonded with a nickel electrodeposit, to form a seal for the 'Nichrome V' coating, which was sprayed on, sintered *in vacuo*, and finally densified by infiltration with the lower-melting alloy 'Nicrobraz'.

(4) *'Inconel'-Diffusion-Bonded Specimens*

The cermets were fitted accurately into an 'Inconel' shell, lightly nickel-plated, pressed into place, and fired *in vacuo*, for 18 hours at 2280°F. (1250°C.), to secure a bond between shell and cermet. (Only three samples were tested.)

(5) *Vacuum-Cast Structures*

The procedure was similar to that described in (4), except that the 'Inconel' tubing, enclosed in a MgO mould, was allowed to melt during firing. (None of the samples prepared by this method was subjected to impact tests.)

It is concluded that, in a strictly literal sense, the objective was achieved, in that a 0·018-in. (0·45-mm.) diffusion-bonded coating of electrodeposited nickel raised the impact strength of the cermet to which it was applied from 2·56 to 21·48 in.-lb. at room-temperature and from 3·36 to 18·96 in.-lb. at 1800°F. (980°C.). It is emphasized, however, that these values should not be extrapolated to infer a tenfold increase for a similarly coated turbine blade. (In this connexion, the factors to be considered in assessing the practical value of the techniques are discussed and suggestions are made as to the mechanism by which improvement was achieved.)

Direct application of brazing alloys was deemed unsatisfactory and, though the infiltrated coatings showed promising structures, no appreciable improvement in impact-resistance was achieved with the composition used.

The limited data derived from tests on cermets with 'Inconel'-diffusion-bonded coatings indicated that appreciably increased impact strength was thus obtained.

High-Temperature Properties of 'Waspaloy' Alloys as Affected by Composition and Heat-Treatment

C. A. HOFFMAN and M. B. HORNAK: 'Elevated-Temperature Combined Stress-Rupture plus Fatigue Strength of 'Waspaloy' having Different Ageing Treatments and/or Molybdenum Contents.'

Nat. Advisory Committee for Aeronautics, Research Memorandum E57K22a, Feb. 25, 1958; 21 pp.

The investigation originated in the observation that three heats of 'Waspaloy' which varied in molybdenum content and had undergone different thermal treatments showed (at 1500°F.: 815°C.) closely similar stress-rupture properties, but differed in both notch-rupture strength and stress-rupture ductility.

The compositions of the respective materials and the thermal treatments are shown in the table on p. 231.

Group	Heat-Treatment	Composition										
		C %	Si %	Ni %	Co %	Cr %	Mo %	Ti %	Al %	Mn %	Fe %	Cu %
A	2 hours at 1975°F. (1080°C.) air-cooled; 16 hours at 1400°F. (760°C.) air-cooled;	0·04	0·57	bal.	14·18	20·10	2·97	2·7	1·25	0·89	0·55	0·12
B	2 hours at 1975°F. (1080°C.); air-cooled;	0·04	0·57	bal.	14·18	20·10	2·97	2·7	1·25	0·89	0·55	0·12
C	4 hours at 1550°F. (845°C.); air-cooled; 16 hours at 1400°F. (760°C.); air-cooled	0·062	0·64	bal.	13·87	19·61	7·32	2·47	1·01	0·74	0·41	0·01

The following observations had been made:

Notching strengthened materials from Groups A and B.

Notching either left unchanged or slightly weakened material from Group C.

Material from Group A showed the lowest, and that from Group C the highest, stress-rupture ductility.

It was considered that, since Group C material had the best stress-rupture ductility but not the highest notch-rupture strength, these two properties might not be directly related, but that the hypothesis might be advanced that where groups of material have comparable stress-rupture properties the one showing the highest stress-rupture ductility and/or notch-impact strength would, when subjected to a combination of stress-rupture and fatigue, take the longest time to failure.

Study of the three groups of 'Waspaloy' was therefore carried out to ascertain whether any correlation existed between combined stress-rupture and fatigue life and stress-rupture ductility and/or notch-rupture strength. The results are presented in this Memorandum.

Fatigue tests were made at 1500°F. (815°C.) with direct tensile cyclic stresses superimposed upon direct tensile mean stresses. Mean tensile stresses were selected (from data on stress-rupture at 1500°F.: 815°C.) to produce stress-rupture failure times of about 10, 100 and 500 hours. Cyclic tensile-stress levels were chosen to equal 12·5–90 per cent. of the mean tensile stresses.

The results revealed no clear relationship between combined stress – rupture + fatigue strength and notch-rupture strength. Group C, which showed a lower notch strength than the other groups had the best combined stress-rupture + fatigue properties.

Stress-rupture ductility of Group C was appreciably better than that of A or B, and that of B was slightly better than that of A. Since Group C had the best combined stress-rupture + fatigue strength, Group B the next best, and Group A the lowest, it is considered that there is some indication of a possible connexion between stress-rupture ductility and the combined-stress properties. No relationship was established between the combined properties and dynamic ductility (ductility at failure in combined stress).

From consideration of the heat-treatments and/or of the compositions of the alloys *per se* (i.e., taking no account of their effects on the basic properties of ductility, etc.) it is concluded that double-ageing treatment improved the combined stress-rupture + fatigue strength of the heat containing 3 per cent. of molybdenum. Increase in molybdenum content, in conjunction with the double-ageing treatment, further improved these properties.

Group C, having a duplex grain structure (which might be expected to have a deleterious effect on resistance to combined stress-rupture + fatigue), was found generally to exhibit the highest combined-stress strength.

Creep of Nickel and Nickel-Copper Alloys

W. D. JENKINS and C. R. JOHNSON: 'Creep of Annealed Nickel, Copper and Two Nickel-Copper Alloys.' *Jnl. of Research, Nat. Bur. Standards*, 1958, vol. 60, Mar., pp. 173–91; *R.P.* 2836.

Effects of temperature on the short-time tensile properties of nickel, 30–70 and 70–30 copper-nickel alloys, and copper have been reported in earlier papers from the National Bureau of Standards. The present report gives extensive information on creep characteristics of the same metals, based on tests made in the course of a research designed to evaluate the rheological properties of the materials over the range −320° to +1700°F. (−195·5° to +926·5°C.).

The compositions of the materials studied are shown in the table on page 232.

The creep tests were made at 300°, 700° and 900°F. (149°, 371° and 482°C.), on initially annealed specimens of all the materials. Test conditions were arranged to permit evaluation of the influence of rate of loading and prior-strain history, on creep characteristics, hardness and contours of the specimens. On the nickel and the two alloys tests were made also at 1200°F. (649°C.). Metallographic

Material	C %	Cu %	Ni %	Co %	Fe %	Mn %	Si %	S %	Zn %	O_2 %	N_2 %	H_2 %	Avge. grain dia. (*c*)
													mm.
Copper(*a*) (OFHC)	—	99·99+	—	—	—	—	—	—	—	—	—	—	0·025
30%Ni-70%Cu	0·023	68·84	29·89	0·04	0·50	0·65	0·003	0·004	0·09	0·001	0·001	0·0002	0·040
70%Ni-30%Cu	0·017	29·71	70·08	(*b*)	0·01	0·01	0·12	0·002	—	0·001	0·0015	0·0003	0·025
Nickel	0·007	0·009	99·85	(*b*)	0·04	0·03	0·11	0·002	—	0·002	0·001	0·0002	0·015

(*a*) The arc spectrum of the copper was examined for the sensitive lines of Ag, Al, B, Be, Co, Fe, In, Ir, Mg, Mo, Na, Ni, Pb, Sb, Si, Sn, Ti, V and Zn. The lines for Ag, Al, Mg and Si were identified and there was some indication of the presence of Fe, Ni and Pb.

(*b*) Not detected. (*c*) Values obtained on specimens prepared from the annealed bars.

examination was carried out on some typical specimens, to correlate changes in structure with other effects associated with creep.

Particular attention was directed to the properties of the alloys in relation to those of the component metals. It was found that initial resistance to flow was increased by alloying, and that maximum flow-resistance was obtained in the 70–30 nickel-copper alloy. The characteristics of the respective materials, and their behaviour in the varying experimental conditions used, are discussed in relation to the theory and mechanism of creep.

Effects of Overheating on Aircraft Gas-Turbine Alloys

J. P. ROWE and J. W. FREEMAN: 'Effect of Overheating on Creep Rupture Properties of 'M-252' Alloy.' *Nat. Advisory Committee for Aeronautics, Tech. Note* 4224, Mar. 1958; 83 pp.

The investigation reported was the third in a series carried out to obtain basic information on the change in creep-rupture properties of high-temperature alloys brought about by overheating in conditions which might occur in the service of gas-turbine blading. (Results of two earlier studies, on 'S-816' and 'HS-31' alloys, were reported, respectively, in *N.A.C.A. Tech. Notes* 4081 and 4083; see abstracts in *Nickel Bulletin*, 1958, vol. 31, No. 5, pp. 138, 139.)

In the tests now reported conditions were again designed to simulate service operation; brief overheating was effected at 1650°, 1800°, 1900° and 2000°F. (898°, 982°, 1038° and 1093°C.).

The material used was the wrought alloy 'M-252'. Most of the tests were made on vacuum-melted material of the following percentage composition: carbon 0·12, chromium 19·22, cobalt 9·73, molybdenum 10·18, titanium 2·4, iron 2·4, aluminium 1·12, manganese 0·1, silicon 0·35, sulphur 0·007, phosphorus 0·002, balance nickel.

Effects of overheating were evaluated in terms of creep-rupture properties at 1500°F. (815°C.), under stresses within the range of its rupture strengths for 80–1000 hour periods. (For the general features of the test conditions, see abstracts of the previous investigations, *Nickel Bulletin, loc cit.*)

The experimental results on the 'M-252' alloy led to the following main conclusion:

Overheating for 2-minute periods to temperatures of 1900° or 2000°F. (1038° or 1093°C.) can, if repeated sufficiently often during the test, substantially increase rupture times at 815°C. For overheating at such temperatures to have a damaging effect on stress-rupture life it is necessary that during the overheat the material should be under a stress sufficient to use up a significant amount of the rupture life. It is even possible for a significant amount of creep damage to be offset during repeated overheating by the increase in rupture time resulting from the temperature effect.

Overheating to 1650° and 1800°F. (898° and 982°C.) in the absence of stress had a harmful effect on rupture life at 1500°F. (815°C.). In the presence of stress the damage caused by such overheating had, however, a much less deleterious effect than was anticipated, due to an unidentified factor which probably has a strengthening effect. It is on this observation that the conclusion is based that, if a damaging effect is to be produced by stress, that stress must be high enough to use up a substantial amount of the rupture life.

Overheating (under cyclic conditions) prior to test does not give the same effects on stress-rupture properties at elevated temperature as results from overheating during test, and it is therefore not possible to use prior overheating to evaluate effects resulting from cyclic temperature conditions during service. Some suggestions are, however, made for a method by which a close approximation of creep damage can be made in terms of percentage of life used up under given conditions. There appears to be no satisfactory means of determining the temperature effect on the basis of commonly available data.

It is emphasized that the above conclusions are subject to certain significant limitations, e.g., the number of overheating conditions studied were relatively limited, the influence of heat-treatment of the alloy and of variation from heat to heat was not investigated, and the mechanism of some of the effects observed is uncertain. In particular, it is important that the indication of improvement or lack of damage resulting from overheating of 'M-252'

under certain conditions should not be accepted, without further investigation, as characteristic of other nickel-base alloys in which the strengthening elements are aluminium and titanium. The general results obtained for all the three alloys which have been used in the overheating studies are considered to be qualitatively reliable, although it is recognized that the magnitude of the effects may vary with the metallurgical variables involved, which should be the subject of closer study.

The report includes a critical comparison of the effects resulting from overheating in the three alloys which have been examined, with consideration of the structurally different character of the respective types.

Thermal Properties of Metals and Alloys: Reference Data

See abstract on p. 211.

Austenitic Steel Castings for High-Temperature Turbine Applications

W. STAUFFER and A. KELLER: 'Austenitic-Steel Castings as Materials of Construction for Gas- and Steam-Turbines.'

Giesserei, 1958, vol. 45, Apr. 24, pp. 229–39.

It has been repeatedly emphasized in the literature that, while the way to improved efficiency in gas- and steam-turbines lies through the use of greater loads and higher temperatures, success in this connexion is governed by availability of materials of construction capable of withstanding the conditions involved. At temperatures up to about 600°C. low-alloy steels and chromium stainless steels have proved satisfactory for structural applications; above that temperature the greater strength and heat-resistance of chromium-nickel austenitic stainless steels must be utilized. Many of these applications (for example, turbine-housings, valves, pipe-fittings, etc.) will necessitate the use of castings, and this paper reviews information on the high-temperature properties and weldability of austenitic steels in cast form.

The four grades of steel considered suitable for this purpose (to which the survey is therefore confined) are those containing chromium 16–19, nickel 9–12, per cent. (with or without niobium-tantalum stabilizing additions) or chromium 15–17, nickel 10–14, molybdenum 1–3, per cent. (also with or without niobium-tantalum). The basis composition of the cast steels is similar to that of the wrought corrosion-resisting grades, but the alloying additions, while similar in kind, are used to different effect, since the molybdenum and niobium contents are intended mainly to increase heat-resistance. For turbine applications experience has shown that alloying additions must be carefully controlled to achieve optimum heat-resistance compatible with minimum sacrifice of other properties. The grain-size of the casting is of great importance.

Discussion of the creep-resistance of cast austenitic steel centres on curves derived from tests at 650°C. (i.e., the average temperature at which the steels would be used in turbines), for times up to 40,000 hours. A 100,000-hour creep strength of at least 2·3 kg./mm.² (1·5 t.s.i.) at 650°C. for an 18–8 type stainless steel is increased to 4·5 kg./mm.² (2·8 t.s.i.) by niobium or molybdenum additions, or to 5 kg./mm.² (3·17 t.s.i.) when both these elements are present. From curves relating creep data for four typical cast steels with values obtained from similar wrought steels, the authors conclude that cast and wrought stainless steels do not differ to any great extent in creep-resistance or, indeed, in the scatter exhibited by the long-time results.

Data on notch impact-resistance of the four steels are based on room-temperature tests on specimens which had been subjected, without load, to high temperatures for periods of up to 10,000 hours. Susceptibility to embrittlement is expressed in terms of the percentage relationship between the final and initial impact-resistance values. These data, compared with those for wrought steels of similar composition, show the initial impact-resistance of the cast steels to be lower (by a quarter to a half) and, since susceptibility of the two grades of steel to embrittlement is approximately equal, values for the cast steels after exposure to service temperatures are, in general, very low (e.g., 1 kgm./cm.²: 7 ft.-lb. after 10,000 hours at 650°C.). The range of scatter shown by these results is far more pronounced for the cast than the wrought steels. The low initial impact-resistance exhibited by the cast steels is ascribed to the influence of a coarse grain size and presence of contaminants at the grain boundaries. Embrittlement is attributed to changes which occur in the austenitic matrix as a result of precipitation brought about by exposure at service temperatures. In this connexion curves illustrating susceptibility to embrittlement after 10,000 hours at 650°C. are correlated with photomicrographs of the steels concerned.

Welding is the technique most generally used in the fabrication of austenitic-steel turbine castings. The tendency of the steels to form coarse grains, and the presence of contaminants and of phases other than austenitic which form at the grain boundaries, are deleterious in this respect. These changed areas either melt prematurely or, under the stresses which arise during welding, cause cracking in the heat-affected zone of the weldment. The coarser the grain, the greater the risk of failure. Photomicrographs of typical grain-boundary precipitates are used to supplement the textual discussion and to illustrate beneficial effects obtainable by plastically deforming the edges of the joint, under load, prior to welding. This process (developed and patented by Escher Wyss A.G.) is intended to break up the grain and so disperse the deleterious grain-boundary constituents.

The paper ends with comments on directions in which work might advantageously be carried out to develop cast austenitic steels having improved creep- and impact-resistance.

Nickel-Chromium Steel for Tubing in Power Plants

A. S. GELMAN *et al*: 'Study of Steel 1Kh18Ni12T as a Tube Material for Power Plants.'

Metallovedenie i Obrabotka Metallov, 1958, No. 3, Mar., pp. 16–24.

Ageing of a titanium-stabilized steel containing chromium 18, nickel 12, per cent., exposed for periods up to 10,000 hours at 600°–750°C. resulted in no embrittlement, and no sigma phase was found. The elevated-temperature strength of both the parent material and of welds made in this steel was also satisfactory after exposure for 3,000 hours in steam conditions at 650°C.

'Croloy 15-15N' Steel for High-Temperature Tubing

J. F. EWING: 'An Austenitic Heat-Resistant Alloy for Severe Tubular Applications at Elevated Temperatures.'

Amer. Soc. Mechanical Engineers, Paper 57-*A*-205, Dec. 1957; 10 pp.

'Croloy 15-15N' has been developed by Babcock and Wilcox Company specifically for use as a high-temperature tubing material. The 'specification' to be satisfied was

Mechanical properties, in the range 1200°–1500°F. (650°–815°C.), superior to those obtainable in 18-8 type chromium-nickel stainless steels currently used for such applications.

Capacity for fabrication into tubular products by conventional hot- and cold-working techniques.

The composition of the steel is closely related to that of 16-13-3 chromium-nickel-molybdenum A.I.S.I. Type 316: tungsten, molybdenum, and niobium + tantalum additions are used to strengthen a 15-15 chromium-nickel base. The preferred percentage composition range is given as: carbon 0·15 max., silicon 0·75 max., manganese 2·00 max., sulphur 0·045 max., phosphorus 0·03 max., nitrogen 0·15 max., chromium 14·75–18·00, nickel 13·50–16·50, molybdenum 1·25–1·85, tungsten 1·00–1·85, niobium + tantalum 0·80–1·30, balance iron.

This paper summarizes the results of intensive tests on the steel, supplemented by information on service experience with commercial heats. The information is given in sections relating to the following phases of the test programme:

(1) Short-time tensile tests at temperatures in the range room temperature to 1500°F. (815°C.).

(2) Creep-rupture tests at 1200°, 1350° and 1500°F. (650°, 730° and 815°C.), involving determinations of the influence of annealing and ageing temperatures and rate of cooling.

(3) Creep tests at temperatures in the range 1200°–1500°F. (650°–815°C.).

(4) Evaluation of the structural stability of the steel

(*a*) by means of tensile and impact tests at room temperature and at 1350°F. (730°C.), after ageing at 1350°F. (730°C.), for times up to 5,000 hours;

(*b*) by comparison of tensile, creep-rupture and impact properties before and after exposure in a commercial superheater at 1340°F. (725°C.) for 7,323 hours.

The results showed that the material can be easily cold- and hot-worked by conventional methods. The creep-resistance and creep-rupture properties of the steel in the range 1200°–1500°F. (650°–815°C.) proved to be superior to those of established austenitic stainless steels, and although solution annealing at 2250°F. (1230°C.) is required to give optimum strength in the range 1350°–1500°F. (730°–815°C.), a temperature as low as 2100°F. (1150°C.) may be used for parts intended for service at 1200°F. (650°C.) or below. Solution treatment at temperatures above 1850°F. (1010°C.) did not affect tensile properties at room temperature, but if a solution temperature below 2250°F. (1230°C.) was used, creep-rupture properties at 1350°F. (730°C.) were deleteriously affected. The temperature of solution treatment exerted no significant effect on creep-rupture strength at 1200°F. (650°C.) or on room-temperature mechanical strength. The condition of the steel after long-term exposure to service temperatures indicates satisfactory structural stability.

Complex Precipitation-Hardenable Austenitic Steel: 'F.V. 520'

'New Stainless Steel to Beat Heat Barrier.'

Materials in Design Engineering, 1958, vol. 47, May, pp. 104–5.

The steel described, known as 'F.V.520', is of the following composition: carbon 0·07, silicon 1·0 max., manganese 2·0 max., chromium 14–18, nickel 4–7, copper 1–3, molybdenum 1–3, titanium 0·5 max., per cent. The information contained in the article is condensed from that published in *Iron and Steel*, 1957, vol. 30, Oct., pp. 487–8.

High-Temperature Materials for Rocket Power Plant

R. C. KOPITUK: 'Materials for 'Hot' Rocket Parts Must Withstand 1700°F. Plus.'

Aviation Age, 1958, vol. 28, Jan., pp. 104–9.

In introducing this semi-popular survey the author outlines the conditions which prevail in the critically hot components of rocket motors (operating on liquid propellants) at temperatures above 1700°F. (925°C.). He then bases his discussion on a table which correlates the components of the rocket motors with the materials of construction used and the properties which indicate their suitability for such applications. The parts considered include the gas

generator, injector head, combustion-chamber extension cone, and uncooled and regeneratively-cooled combustion chambers.

Temperatures in the gas generator approach 1900°F. (1035°C.): ceramic coatings form a suitable insulation for high-strength low-temperature materials if the operating life is short (e.g., 30 seconds), but for longer periods the coating necessary for effective insulation becomes too heavy except in cases where the increased oxidation- and corrosion-resistance so obtained is essential.

Depending on the propellant used and the location, temperatures in the region of the injector head range from −420° to +2500°F. (−250° to +1370°C.). High-temperature strength and resistance to oxidation and corrosion are often essential in the components, but to meet varying service conditions the materials employed have ranged from low-alloy and stainless steels to nickel-base and other high-temperature alloys and steels. Use of nickel-base brazing alloys ensures leak-proof joints in the injector partitions which separate the highly reactive propellants.

In discussion of the combustion-chamber extension cone, and of the severe conditions which are inevitably associated with the expanding gases entering from the combustion chamber, mention is made of the various metals, cermets or ceramics used as protective cratings. Similarly, the uncooled combustion chambers, which are in operation only for short durations, and the regeneratively cooled thrust chambers, where total operating life can be several hours, are subjected to a combination of high-temperature, oxidizing, corrosive and erosive conditions. These entail use not only of high-strength materials such as 'Inconel' or '17-7 PH' steel, but of protective coatings which, as indicated in the article, range from a nickel braze or aluminium dip to sprayed alumina and zirconia powder.

Nickel-containing Materials in Television Equipment

See abstract on p. 224.

Nickel-base High-Temperature Brazing Alloys

'High-Temperature Brazing Alloys.'

Metal Industry, 1958, vol. 92, June 27, p. 530.

This note relates to four commercial brazing alloys, the composition and flow temperatures of which are given in the next column.

Alloy	Ni %	Cr %	Si %	B %	Flow temperature in dry hydrogen °C.
'CM.50'	93·25	—	3·5	2·25	1055
'CM.52'	91·25	—	4·5	2·9	992
'CM.53'	82·0	7·1	4·5	2·9	996
'CM.56'	71·0	15·0	4·5	3·5	1030

The alloys, which are manufactured (in the form of powders or cast rods) by Dewrance and Company Ltd., are claimed to have the strength, resistance to oxidation, erosion and corrosion, and the flow characteristics requisite for high-temperature service. (The shear strength of a stainless-steel joint made with such brazing alloys is stated to be greater than 20 and 10 t.s.i. (31·5 and 15·8 kg./mm.²) at room temperature and at 500°C., respectively).

'Alloy CM50' is recommended for applications where ductility is of primary importance. 'Alloy CM52' is particularly resistant to attack by liquid sodium, mercury and mercury vapour, and is used where maximum penetration of the joint is required. Similar wetting characteristics are exhibited by 'Alloy CM53' which, in general, has better corrosion-resistance. The 'CM56' grade shows the highest corrosion-resistance: this alloy is, however, less fluid than the others of the series and therefore more difficult to use.

The alloys, in powder form, can be applied to the surface of the work in the form of a paste or spray. A hydrogen atmosphere is generally recommended for brazing stainless steel, 'Nimonic 75' or cobalt-base alloys, and burnt town's gas for mild steel: vacuum brazing is, however, essential for joining 'Nimonic 80' and 'Nimonic 90'.

Brazing Alloys for High-Temperature Applications

A. M. SETAPEN: 'Brazing-Filler Metals Meet High-Temperature Needs.'

Iron Age, 1958, vol. 181, May 8, pp. 110–11.

The information given in this short article coincides in part with that reported at length by SISTARE and McDONALD (*Welding Research Council Bull. No.* 30, Sept. 1956; abstract in *Nickel Bulletin*, 1958, vol. 31, No. 3, p. 93).

The following alloys to which no reference was made in the W.R.C. report are briefly evaluated in this article: silver-copper-lithium; manganese-nickel; nickel-chromium-silicon-boron-(iron).

Addition of small amounts of lithium (about 0·2 per cent. is typical) has been found to improve the fluidity and wetting characteristics of many standard brazing alloys: a silver-lithium alloy is finding increasing application in brazing stainless steel (its flow temperature, for example, corresponds to that optimum for heat-treatment of '17-7 PH' stainless steel). The manganese-nickel alloy is at present under consideration for brazing heat-exchange parts, rocket-motor components, and other parts: it is now available as powder or strip.

Reference is made also to the value of nickel-boron-base alloys, which are particularly useful as retaining a high degree of hardness and strength in the range 1600°–1800°F. (870°–980°C.). This type has recently been considered in greater detail by HOPPIN (see *Welding Jnl.*, 1957, vol. 36, Dec., pp. 528s–30s: *Nickel Bulletin*, 1958, vol. 31, No. 3, p. 92).

Vacuum Brazing of High-Temperature Alloys

E. G. HUSCHKE and G. S. HOPPIN: 'High-Temperature Vacuum Brazing of Jet-Engine Materials.'
Welding Jnl., 1958, vol. 37, May, pp. 233s-40s.

Although high-temperature brazing (with nickel-chromium-boron filler materials) has already made possible fabrication of many lightweight structures in materials which could not be otherwise fabricated, it has not been found possible to render hydrogen or any of the other protective brazing atmospheres sufficiently inert to permit successful brazing on many of the complex high-temperature alloys. An additional problem arises because hydrogen brazing is completely incompatible with some of the highly reactive metals now being considered for elevated-temperature applications, e.g., niobium and titanium.

The subject is under intensive study in the laboratories of various organizations associated with high-temperature engineering projects, among which is the General Electric Company Aircraft Gas Turbine Division in Cincinnati, Ohio. This paper reports results of vacuum-brazing experiments carried out by the G.E.C. laboratory during the past two years. The investigations have included study of maximum-pressure requirements for brazing various alloys, gas evolution of metals in vacuum, strength of vacuum-brazed *vs.* hydrogen-brazed joints, and alternative methods for joining high-temperature alloys which form oxide films in hydrogen.

The materials used have been representative of 'superalloys' readily brazed in purified hydrogen, types which are difficult to braze in such atmospheres due to formation of non-reducible surface oxides of aluminium and titanium, and other jet-engine materials of typical compositions (used, in this investigation, only for brazing-alloy-flow tests). The two brazing alloys used were, respectively, of the nickel-chromium-boron and nickel-chromium-silicon types. Full composition of all the materials are tabulated. The three types of apparatus used for vacuum brazing are described and full details are given of experimental conditions set up for all the tests.

The most significant conclusions to be gained from consideration of the results, including comparison of the properties of joints brazed *in vacuo* and in hydrogen (for alloys on which both methods could be used) are as follows:

The maximum allowable pressures for vacuum brazing high-temperature alloys containing titanium and aluminium are a function of the alloy content: on three typical materials studied they were found to vary from 2 to more than 35 microns. All the twelve representative alloys tested brazed well at 0·2 microns pressure.

Gas evolution from materials heated in vacuum was found to vary widely according to the method of melting which had been used in their production, and also with weight/surface ratio.

For a material typical of alloys readily brazed in hydrogen, strengths of vacuum- and of hydrogen-brazed joints were found to be identical. For an alloy not readily brazeable in hydrogen, vacuum-brazed joints were the stronger, even when specialized technique had been used in hydrogen brazing (*see next paragraph*).

Study of alternative methods of brazing the 'difficult' alloys showed that titanium-and aluminium-bearing types can be brazed in hydrogen by:

(*a*) Plating the surfaces which are to be brazed with a metal the oxides of which are reducible by hydrogen (e.g., with nickel or iron).

(*b*) Use of certain fluxes, of which sodium fluoride has proved to be the most suitable.

(*c*) Pre-oxidizing and leaching the surfaces which are to be brazed, a process which involves first forming an oxide film in a 'wet' (−40°F.; −40°C. dewpoint) hydrogen atmosphere, and subsequently leaching out this titanium- and aluminium-oxide film by means of a nitric-hydrofluoric acid pickle, leaving the surface essentially free of titanium and aluminium. Brazing of the surface in that condition can be carried out in purified hydrogen.

(*d*) Pre-placement of the brazing alloy, involving flame spraying, fusing of the sprayed coating to the base surface, and brazing in dry hydrogen.

Each of these methods is to some extent successful, but each has disadvantages: both aspects are critically discussed.

Brazing of 'Nimonic' Alloys and Stainless Steels (1)

A. CIBULA: 'The Soundness of High-Temperature Brazed Joints in Heat-Resisting Alloys. The Influence of Composition and Brazing Conditions on the Spread of Molten Brazing Alloys.'
Brit. Welding Jnl., 1958, vol. 5, May, pp. 185-201.

Although brazing, with its many advantages, has found widespread application in a variety of fields, little systematic investigation has been made of the fundamental factors involved in the production of sound joints by this method. Previous work has been confined largely to the development of brazing techniques, alloys and fluxes which were suitable only for specific applications, but investigations on such an empirical and *ad hoc* basis have not always led to consistent high quality in the joints. The work recorded in this paper was therefore carried out in an attempt 'to identify the factors which determine the optimum brazing conditions for various types of joint'. Although the author's primary object was study of these factors in relation to brazing of austenitic stainless steel and nickel-chromium alloys, some of the facts established may be regarded as more generally applicable. (The information now published was earlier made available to members of the British Non-Ferrous Metals Research Association, in three confidential reports issued in 1955 and 1956.)

The basis materials, used in the form of 0·048-in. (0·12-cm.) thick sheet, were: (1) 18-10 chromium-nickel niobium-stabilized stainless steel; (2) 'Nimonic 75' (chromium 18-20, iron 5 max., titanium 0·2-0·6,

per cent., bal. nickel); (3) 'Nimonic 90' (chromium 18-21, cobalt 15-21, iron 5 max., titanium 1·8-3, aluminium 0·8-2, per cent., bal. nickel).

Of the 16 brazing alloys employed, 12 were commercial high-temperature materials: nickel-base (Ni-Cr-B-Si-Fe, Ni-Si-B, Ni-Mn-Pd); silver-base (Ag-Pd, Ag-Pd-Mn, Ag-Cu-Pd); cobalt-base ('Stellite 100'); or manganese-base (Mn-Ni-Cr). The remainder were of copper base (Cu-Ni-Si, Cu-Si-Cr, Cu-Ni-Mn, Cu-Ni-Cr-Co), and pure copper and silver were also used. A total of 25 fluxes were evaluated.

All the brazing tests were carried out in a hydrogen atmosphere, on single square lap joints with clearances of up to 0·10 in. (0·25 cm.). Each finished joint was radiographed to determine its soundness. Full details are given of experimental apparatus and procedure.

The scope of the programme and some of the results are outlined below.

(1) Removal of Surface Oxides

Removal of the deleterious refractory oxide scales which form on heat-resisting alloys at high temperatures was studied by

(*a*) attempts to braze the materials in a reducing (hydrogen) atmosphere at temperatures up to 1300°C., and

(*b*) evaluating the effects of fluxes, at 1120° and 1200°C., on the spread of brazing alloy over strips heavily oxidized before, or moderately oxidized after, application of the flux, or lightly oxidized by heating in impure hydrogen.

Results:

(*a*) Austenitic stainless steel, and 'Nimonic 75' and other heat-resisting alloys containing little or no aluminium and less than 1-2 per cent. titanium could be brazed, without a liquid flux, in purified hydrogen (containing about 10^{-4} vol. per cent. of moisture), at temperatures above 1000° and 1100°C., respectively. Oxide films on 'Nimonic 90' and other alloys containing aluminium could not be reduced in hydrogen without a flux unless they were first plated with metals (such as copper, nickel or chromium) which form more easily reducible oxides.

(*b*) Boric oxide proved the most active flux. It can be safely heated for prolonged periods on stainless steel, or, in the case of 'Nimonic 75', for periods of up to 30 minutes at 1200°C., but it caused severe erosion of 'Nimonic 90'. Borax was less harmful, and it is considered that erosion and embrittlement under severe conditions can be controlled by limiting the amounts of flux and brazing alloy used to two or three times the volume of the capillary space.

(2) Study of Spreading Characteristics

Spreading tests were made on resistance-heated strips of the basis materials, to determine the optimum-spreading temperature of the various brazing alloys. In this connexion the influence of the following variables was evaluated:

(*a*) Composition of the brazing alloy;

(*b*) Presence of fluxes;

(*c*) Use (on 'Nimonic 90') of self-fluxing brazing alloys containing boron, phosphorus or lithium;

(*d*) Surface finish of the basis metal.

The degree to which the basis metal was eroded during brazing was also determined.

Results:

(*a*) Presence, in the brazing alloy, of at least 5-20 per cent. of an element soluble in the basis metal at the brazing temperature was found to be conducive to the attainment of a low spreading temperature, although excessive alloying with the basis metal could hinder spreading (e.g., nickel-boron and manganese-base alloys).

(*b*) Variation of rate of spreading with temperature was often greater in the presence of a flux, but with the flux spreading could in some cases be more rapid and less hindered by inter-alloying.

(*c*) All the self-fluxing alloys proved severely erosive.

(*d*) Though the ability of the molten alloy to spread was dependent, to a certain extent, on the surface finish of the basis metal, the effect of temperature was usually more important. (In this connexion optimum spreading temperature and erosive characteristics of each alloy are illustrated.)

(3) Factors Affecting Soundness of the Joints

A dozen or more lap joints in stainless steel and 'Nimonic 75' were brazed with each alloy, in a hydrogen atmosphere, at temperatures above and below the spreading temperature, and, in some cases, at two rates of heating. In addition, lap joints in all the basis materials were brazed in hydrogen, using borax as flux, and, employing, in some cases, brazing conditions which in the absence of a flux had resulted in a high degree of soundness. The data obtained yielded information on the following aspects:

(*a*) The joint-filling process and causes of unsoundness;

(*b*) Influence of joint design and mode of heating;

(*c*) Relation between spreading temperature and optimum brazing temperature.

Results:

(*a* and *b*) The joint-filling properties of the respective brazing alloys are recorded. The principal cause of unsoundness in capillaries of large clearance was found to be uneven heating, which resulted in the filling of the hotter parts of the joint first, so that the molten metal could not then penetrate the isolated pockets of gas, flux or oxide in the cooler parts. Reduction in joint clearances retarded capillary penetration, the temperature gradients were able to decline before the joint was filled, and unsoundness was thus reduced. Too narrow a clearance will, however, result in the joint becoming

choked by alloying. The range of capillary clearances which obviate the deleterious effect of uneven heating is critically dependent on brazing conditions, and it is concluded that optimum conditions for the production of sound joints are a combination of suitable joint design and a method of heating which will permit rapid melting and uni-directional flow of the brazing alloy.

(*c*) The presence of a flux greatly increased unsoundness.

(*d*) Optimum brazing temperature was found to be governed by the brazing process used. Joints containing long narrow capillaries may be best filled at temperatures above the spreading temperature, whereas unsoundness in unevenly heated joints of large clearance would probably be reduced by use of brazing temperatures well below the spreading temperature.

The report is particularly well supported by tables, graphs and photomicrographs, and includes diagrams of the high-temperature brazing furnace used, the design of the brazed joints, and the apparatus employed in the spreading tests.

Brazing of 'Nimonic' Alloys and Stainless Steels (2)

E. V. BEATSON: 'Brazing in Controlled Atmospheres and *in Vacuo*.'

Brit. Welding Jnl., 1958, vol. 5, Apr., pp. 137–43.

Pre-requisites for the production of a satisfactory brazed joint are

(i) that the filler metal should readily 'wet', and
(ii) that it follow a capillary path between the two metal surfaces.

These two conditions are met only if the surfaces of the parts to be joined are clean and free from oxides.

In practice four methods are employed to remove surface oxides during brazing: use of fluxes, and brazing in reducing atmospheres, in inert gases or *in vacuo*. The use of special atmospheres is the technique discussed in this paper.

The author introduces his discussion of factors of importance in brazing by a review of the various reducing atmospheres used: the exothermic and endothermic types of town's gas, hydrogen and cracked ammonia. In all of these hydrogen is the active reducing agent, used in some cases in conjunction with carbon monoxide. Attention is directed to the possibility of decarburizing or carburizing when using town's gas and to the more effective reduction of oxide which may be achieved by increasing the gas/air ratio.

In a hydrogen atmosphere, reduction of the oxide takes place with formation of water; when the ratio of hydrogen to water is in equilibrium for the particular metal oxide at the particular brazing temperature, the reducing reaction will cease. In this connexion, taking the dewpoint as a criterion of the water content of the hydrogen, the author discusses curves which show variation, with temperature, of the equilibrium dewpoint for oxides of iron, tungsten, molybdenum, zinc, chromium, manganese, vanadium, silicon, titanium, aluminium, zirconium and beryllium. It is emphasized, however, that the dewpoint of hydrogen is not the only criterion for satisfactory reduction of oxide: reference is made to the problem of atmospheric contamination and to the part played by oxygen content and temperature of brazing. The theoretically derived curves referred to above, which indicate the temperature at which the reducing reaction is at equilibrium, are thus related to practical brazing conditions.

The harmful effect of even trace amounts of contaminants (e.g., of the order of 0·03 per cent. of oxygen and water vapour) is cited as the cause of unsuccessful attempts to establish production conditions for brazing 18–8 type stainless steels in a cracked-ammonia atmosphere, although laboratory tests had shown that such materials could be copper-brazed at 1150°C. in hydrogen with a dewpoint of −25° to −20°C.

Little published information is available on the possibility of brazing, in a hydrogen atmosphere, materials containing several alloying constituents which form complex surface oxides, e.g., stainless steels or high-nickel alloys containing substantial amounts of titanium, silicon and aluminium. Knowledge is lacking as to the content of such elements at which their presence becomes critical, or their effects in given combinations. As a practical aid to deduction of the influence of these variables, the author therefore gives details of successful and unsuccessful experience in brazing various types of alloy on which complex oxides are present, e.g., alloys of the 'Nimonic' series, and unstabilized and stabilized austenitic steels. Particulars are given of brazing conditions and of the percentages of alloy elements present in the respective materials.

From analysis of these data, the following conclusions are drawn:

An alloy which contains a reasonably large proportion of a metal which has an oxide much more stable than the oxides of the other elements present appears to behave as though this metal were the main constituent, e.g., an '18–8' stainless steel appears to follow very closely the behaviour which would be theoretically predicted for pure chromium.

Even very small additions of a metal having a very stable oxide exerts a positive effect on reduction of oxide. The influence of very small amounts (e.g., 0·5 per cent.) can, however, be offset by comparatively small improvements in the dewpoint of the atmosphere, although such alteration would be quite inadequate if the stable oxide were present in large quantities.

Additions of about 2 per cent. of metals having very stable oxides appear to have a major effect, although it is not established whether, even at this low percentage, such elements are beginning to act as though they were the main constituents of the alloy. It appears likely also that the form in which the alloying constituent is present will have a bearing on its effect. More information is, however, required on all these points before firm conclusions can be drawn.

Brief mention is made also of brazing in reducing atmospheres at lower temperatures.

In recent years considerable research has been centred on the application of vacuum techniques to brazing those alloys which have proved difficult or impossible to braze in hydrogen (e.g., austenitic stainless steels and the high-temperature 'Nimonic' alloys). Information is presented on typical pressures theoretically required for dissociation of the metallic oxides encountered with such materials, and on the results of 'wetting' and 'spread' tests on 18-8 stainless steel, 'Nimonic 90' and titanium. It is tentatively suggested that the mechanism of oxide removal is not that of dissociation, but of absorption, by the alloy, of oxygen from its oxide.

In a brief note the author emphasizes the necessity for careful control of inert atmospheres during brazing, and the paper ends with a short résumé of factors relating to the flow of the brazing metal into close-fitting joints.

Welding of 'Inconel X' Sheet

J. HARRIS, M. D. BELLWARE and J. J. RILEY: 'Spot Welding of 'Inconel X' in Thickness Range of 0·032 to 0·188 in.'

Welding Jnl., 1958, vol. 37, June, pp. 570–8.

Earlier published information on spot welding of 'Inconel X' has covered the thickness range up to 0·062 in. (0·155 cm.), but use of the method recommended for material of these gauges indicated that for thicker sheet some modification of technique was essential. In this paper full details are given of a method which involves a dual-pressure and a dual-current cycle. The weld is formed during application of the weld force, and defects (porosity) are prevented by forge force in the temper-current period. Using this procedure, porosity was, in most instances, reduced to a point undetectable by X-ray examination. A chart illustrates the design, operation and terminology associated with the new process, and full recommendations are made for spot-welding of sheet in thicknesses ranging from 0·032 to 0·143 in. (0·08 to 0·357 cm.). It is recommended that particular attention be given to surface preparation, using, after degreasing, a pickle solution containing nitric and hydrofluoric acids.

Welds made by the technique described are stated to meet all the requirements of U.S. specification *MIL-W-6858A*, of which details are given in the paper.

Formation of Carbide and Sigma Phases in Austenitic Welds

Y. B. MALEVSKII and B. I. MEDOVAR: 'Secondary Carbide and Formation of Sigma Phase in Welds of Stabilized Austenitic Steel of the 25-20 Type.'

Avtomat. Svarka, 1957, vol. 10, Sept.–Oct., pp. 86–94.

Report of electron-microscope study of the formation of carbide and sigma phases in welds made in steel containing chromium 25, nickel 20, per cent. It is shown that secondary carbides precipitated in the weld during cooling after welding are of irregular shape, with dimensions of the order of 300–800Å. Prolonged exposure in the temperature range 650°–900°C. leads to formation of larger amounts of secondary carbide (e.g., in the form of cubes or prisms). The authors propose a mechanism to explain formation of sigma phase in austenitic welds.

Elevated-Temperature Properties of Welds in Steels and Alloys

H. W. VOORHEES and J. W. FREEMAN: 'The Elevated-Temperature Properties of Weld-Deposited Metals and Weldments.'

Amer. Soc. Testing Materials, Special Tech. Publn. No. 226; 223 pp.

Published by the Society, Jan. 1958. Price $5.50.

This is the seventh in a series of publications designed to make available, in individual volumes, data on the high-temperature properties of various types of material. The whole series is being prepared and issued under the auspices of the A.S.T.M./A.S.M.E. Joint Committee on Effect of Temperature on the Properties of Metals, and the information given has been assembled from many sources, to which references are given.

The data presented (in tabular and graphical form) relate to properties reported for specimens taken entirely from weld-deposited metal and for cross-weld specimens which included both basis metal and weld deposit. The materials to which reference is made are divided into groups according to the principal alloying elements, and, where appropriate, information is given on the heat-treatment to which the materials were subjected. The report includes curves summarizing (as a function of temperature) tensile strength, elongation, reduction in area, stresses for rupture in 100, 1,000, 10,000 and 100,000 hours, and creep strengths for secondary creep rates of 0·0001 and 0·00001 per cent. per hour. The properties of the welds are related to those characteristic of the basis metals by curves derived from data on unwelded material recorded in previous A.S.T.M. Special Technical Publications.

The groups of material covered are shown below.

(1) *Carbon Steels*

(2) *Alloy Steels*
- Mo
- Cr-Mo
- Cr-Mo-V
- Cr-Mo-Nb

(3) *Stainless Steels*
- 18-8 Cr-Ni (+Ti and/or Nb)
- 18-8 Cr-Ni-Mo (and modifications)
- 25-12-Cr-Ni
- 27-9 Cr-Ni
- 25-20 Cr-Ni
- 15-35 Cr-Ni
- '17-4 PH' and '17-7 PH'

(4) *High-Temperature and Super-Strength Alloys and Steels*

'19-9 DL'
'15-15 N'
17-14 Cu-Mo
'A-286'
'N-155'
'S-816', 'S-590' and 'S-588'
'Inconel', 'Inconel W' and 'Inconel X'
'Hastelloy C', 'Hastelloy X'
'HS-25', 'HS-30', 'HS-31'
'16-25-6'
Ni-Cr 50-10 (+Nb/Ta)

Oil-Ash Corrosion of Stainless Steel: Inhibitory Additives

R. C. AMERO, A. G. ROCCHINI and C. E. TRAUTMAN: 'Small-Scale Burner Tests to Investigate Oil-Ash Corrosion.' *Amer. Soc. Mechanical Engineers, Gas-Turbine Power Conference and Exhibit*, Mar. 1958, *Paper* 58-*GTP*-19; 12 pp. + figures.

The search for means of preventing or minimizing the severe corrosion of blading and other components in gas turbines operating on residual fuel oils has been concerned, *inter alia*, with development of additive media which, by formation of high-melting compounds with the vanadium pentoxide present in the fuel ash, would ensure that the deleterious fluxing effect of the V_2O_5 would operate only at temperatures above those encountered in critical parts of the turbine. (Reference to other proposed remedies is made by SACHS in a comprehensive review paper on oil-ash corrosion published in *Metallurgia*, 1958, vol. 57, Mar., Apr. and May; see abstract in *Nickel Bulletin*, 1958, vol. 31, No. 7, pp. 194-5.)

The present paper records the results of a large number of tests carried out in small-scale (micro-) burners, to assess the effect of various additives in inhibiting oil-ash corrosion of A.I.S.I. Type 310 25-20 chromium-nickel stainless steel.

The steel, in the form of discs 1 in. (2·5 cm.) in diameter, was exposed for 100 hours at 1450°F. (787°C.) to the combustion gases from residual fuel oil containing 150-200 p.p.m. of vanadium. The additives evaluated (oil-soluble substances, aqueous solutions and finely divided powders) were stirred into the oil prior to its introduction into the burner. On completion of each test the specimens were weighed and de-scaled: the weight of the scale removed was regarded as 'deposits', and the degree of corrosion was determined by the difference in weight before test and after de-scaling. To assess the value of the test in relation to service conditions, comparative tests were carried out in a full-scale combustor.

The results are given in tables and curves, and the additives which proved most effective as inhibitors are grouped according to the total cost involved in their use. Details are given of combinations giving best results and of optimum additive/vanadium ratios of such mixtures. The results of tests made in the micro-burner were found to show good agreement with data derived from the commercial-scale experiments.

Many of the additives substantially reduced corrosion of the steel: the most effective media (which included some not previously reported in the literature) contained one or more of the following elements: magnesium, manganese, potassium, sodium, rare earths, strontium, thorium, phosphorus, tungsten, nickel, tin and zinc. (Certain combinations of additives were far more effective than the same additives alone: for example, rare-earth and sodium naphthenates; manganese naphthenate and potassium carbonate; manganese naphthenate and synthetic sea water.) Reduction in corrosion was found not to be directly proportional to the concentration used, and the first increment of additive apparently achieved a greater degree of inhibition than successive additions. The presence of synthetic sea water and other materials containing sodium and/or potassium reduced attack by the oil ash and enhanced the effectiveness of other inhibitors.

Oil-soluble compounds of the elements tested had the disadvantage of being more expensive than inorganic compounds or minerals and did not necessarily give better results. By way of relating performance to economic factors, it is stated that micronized talc, potassium permanganate and magnesium oxide substantially reduced the corrosion rate at estimated costs, respectively, of 1, 11 and 0·8 cents per barrel of fuel oil.

See also

Gas Turbines Operating on Inhibited Fuel Oils

B. O. BUCKLAND: 'The Effect of Treated High-Vanadium Fuel on Gas-Turbine Load, Efficiency and Life.'

Amer. Soc. Mechanical Engineers, Gas-Turbine Power Conference and Exhibit. Mar. 1958, *Paper* 58-*GTP*-17; 15 pp.

The work reported in this paper is an extension of that carried out earlier by the author on gas turbines operating, under intermittent conditions, on residual fuel oil treated with a water-soluble inhibitor (BUCKLAND and SANDERS, *Trans. Amer. Soc. Mechanical Engineers*, 1955, vol. 177, pp. 1199-209). Subsequently it became necessary to operate the turbines continuously for about 80 hours and tests were run on four inter-cooled regenerative gas turbines of similar design, in order to establish the effect of using various magnesium-inhibited residual fuels under these different conditions. The present paper 'summarizes the additional data obtained and attempts to state some approximate rules concerning the effect of the deposits on the nozzle-flow areas, the load and the efficiency'.

Three series of tests were run, under intermittent and continuous conditions, for varying periods, with fuels containing varying amounts of vanadium. In all cases a magnesium-containing inhibitor was used.

Full details are given of the results obtained. The main conclusions are as follows:

The use of residual fuel oils containing more than 300 p.p.m. of vanadium will cause no more corrosion in the critical parts of turbines operating at 1450°–1500°F. (790°–815°C.) than oil containing 80 p.p.m. of vanadium, provided that in both cases the fuel is de-salted and treated with $MgSO_4$ solution. Comparison of the first-stage nozzle and blades of the oil-burning turbine with those of a gas-burning unit, after similar periods of service, showed little difference in the condition of the parts. Loss in efficiency of turbines operating on inhibited vanadium-containing fuel, relative to those operating on natural gas, is ascribed principally to the deleterious effects of deposits. Intermittent service with residual oil fuel was found to be less troublesome than continuous service, since oil-ash deposit is removed on shutdown. Proposals are made for conditions in which continuous operation on residual oil fuel would be possible.

Cheaper, more efficient, additives (e.g., finely-divided MgO or $Mg(OH)_2$) may eventually be developed and contribute much to solution of the problem of ash corrosion.

Influence of Sulphur-containing Gases on Fatigue Strength of Austenitic Steels

A. B. RYABCHENKOV and E. L. KAZIMIROVSKAYA: 'Fatigue Strength of Austenitic Steels under Conditions of High-Temperature Gaseous Corrosion.'
Metallovedenie i Obrabotka Metallov, 1958, No. 3, Mar., pp. 6–10.

The fatigue strength of two austenitic nickel-chromium steels was measured at 650°C., in air and in air containing sulphur dioxide, with or without water vapour. The presence of 0·3 per cent. of SO_2 caused a drop of 10–15 per cent. in the fatigue strength, by comparison with the value recorded for the tests in pure air, and SO_2 contents of 0·3–5 per cent. caused further deterioration. The fall is attributed to pitting in the presence of the sulphur-containing gas. Increased moisture tended to counteract the effect of SO_2, and in atmospheres corresponding to those typical of the products of fuel combustion (0·3% SO_2+6% H_2O) there was practically no drop, by comparison with the strength in air.

'MicroMach': High-Strength Chromium-Nickel Stainless Steel

'Ductile Stainless Work-Hardens for Extra Strength.'
Iron Age, 1958, vol. 181, May 29, pp. 88–9.

Although the strength properties of high-carbon relatively low-nickel steel of the 17-7 (A.I.S.I. Type 301) grade are well recognized as useful for structural purposes, the full potential of this steel has not been commercially exploited because of its comparatively poor ductility in the cold-worked condition. It has been found, however, that addition of nitrogen, in conjunction with low nickel content, tends to counteract the deleterious effects of work-hardening and this article gives details of a new steel developed on the basis of this combination. The material is the result of collaboration between two groups of U.S. steelmakers and Battelle Memorial Institute.

The steel is essentially a modification of the 17-7 grade, and is intended mainly as a structural material for aircraft applications: nominal composition is given as carbon 0·08–0·12, nitrogen 0·10–0·15, chromium 17–17·6, nickel 6–6·5, per cent. It is stated that, in addition to its improved ductility in the cold-worked condition, the 'MicroMach' steel compares favourably with the Type 301 grade at elevated temperatures and that it is also superior in this respect to the semi-austenitic precipitation-hardenable types and to martensitic stainless steels. It is noted, however, that there is a wide difference in properties of the steel in the longitudinal and the transverse directions: in the longitudinal direction it is readily formable, but in the transverse direction forming can be effected only by the use of generous bend radii. In the extra-full-hard condition the steel is satisfactorily weldable, provided that precautions are taken to prevent recrystallization and its deleterious effects on properties.

The article includes tabular data on the room-temperature properties of 'MicroMach' after varying degrees of cold reduction: comparison is made with Type 301 stainless steels.

Corrosion-Resisting Nickel-Molybdenum-base and Other Nickel Alloys

G. R. BARROW: 'Uses of Nickel-Molybdenum Alloys in the American Chemical Industries.'
Chemische Rundschau, 1957, vol. 10, Dec. 16, pp. 561–4.

The paper is intended to provide a background against which the chemical engineer may select corrosion-resisting materials for some specific applications. The author deals mainly with the alloys of nickel-molybdenum base, describing the properties and some of the applications of the 'Hastelloy' alloys of the 'A', 'B', 'C' and 'F' types. Reference is made also to the nickel-silicon-base alloy 'Hastelloy D'.

There is brief comment also on the properties and uses of some cobalt-base materials, among which a cobalt-chromium-tungsten-nickel alloy is outstanding in its combination of heat- and corrosion-resistance. Attention is directed to the wear- and corrosion-resisting qualities of cobalt-chromium-tungsten compositions.

Typical mechanical properties of alloys of the various groups are listed, and the paper includes short notes on fabrication techniques suitable for the respective types of material. This final section includes reference to welding procedures.

Cupro-Nickel Alloys:
Properties, Fabrication and Applications

See abstracts on p. 221.

Stainless-Steel Bars and Billets:
Standard Specifications

AMER. SOC. TESTING MATERIALS: 'Proposed Tentative Specifications for Hot-Rolled and Cold-Finished Corrosion-Resisting Chromium - Nickel - Manganese Steel Bars.'
Contained in Report of A.S.T.M. Committee A-10 on Iron-Chromium, Iron-Chromium-Nickel and Related Alloys.'

A.S.T.M. Preprint 6, June 1958, pp. 4–8.

The chemical requirements for bars (of various shapes) and rounds are as shown in the table below.

Requirements laid down include finish, mechanical properties in various conditions and sizes, and dimensional tolerances.

'Proposed Revised Standard Specifications for Corrosion-Resisting Steel Billets and Bars for Re-forging', *ibid.*, pp. 9–12,

Covering 20 grades of chromium-nickel, and 13 grades of straight-chromium stainless steels, also two types of medium-chromium steel containing small additions of molybdenum.

Stress-Corrosion Cracking of Austenitic Steels:
Relevant Chemical Factors

H. H. UHLIG and J. LINCOLN: 'Chemical Factors Affecting Stress-Corrosion Cracking of 18–8 Stainless Steels.'

Jnl. Electrochemical Soc., 1958, vol. 105, June, pp. 325–32.

Transgranular cracking of austenitic stainless steels is liable to occur whenever such materials are exposed, in a stressed condition, to critical chemical environments. Although chlorides are the common constituent of a variety of media which cause cracking, it would appear that their presence is not essential. Transgranular cracking of 18–8 chromium-nickel steel has been observed, for example, in caustic-soda solutions at 350°C. under pressure; in acid sulphite cooking liquors; in 12 per cent. hydrofluoric acid + 0·2 per cent. fluosilicic acid at 80°C., also in molten NaOH at 370°C. Cracking of the same type of steel has been found also in hot water containing very little chloride, in steam condensate containing less than 0·5 p.p.m. total solids, and in cooling waters containing 25 p.p.m. or more of chloride. It has been suggested that oxygen is necessary for cracking of the steel in hot water or in steam containing small amounts of chloride, but a case has been reported of cracking of severely cold-worked 18–8 steel exposed to hot pure water. The present authors refer to the literature reporting these varying observations and point out that many other examples could be quoted, illustrating the complexity of the problem and the comparatively wide range of conditions in which such cracking can occur.

Failure of this type can occur in all the common varieties of 18–8 chromium-nickel steel, including stabilized, molybdenum-containing and extra-low-carbon grades, and may be found also in the higher-nickel steels, e.g., 25–12 and 25–20 chromium-nickel types. Time to onset of cracking can vary, from a few hours in severe conditions, to years in milder conditions.

Remedial measures which may be considered are: (1) modification in environment, (2) metallurgical changes, or (3) relief of residual stress. The last-named method is usually only temporarily beneficial: the metallurgical approach will be the subject of a later report; method (1) change of environment, is the subject of the present paper.

Since boiling 42 per cent. magnesium chloride is known to be a rapid and effective test medium, this type of solution was employed in the experiments described, which were designed to demonstrate chemical factors affecting time of cracking, and to provide data from which a plausible mechanism of stress-corrosion cracking of austenitic steels could be developed.

Among the aspects studied were the following: rate of corrosion, effect of rate of stressing on time-to-cracking; effect of adding varying amounts of an acid (HCl) or a base (NaOH) to the chloride test solution; the influence of anodic or cathodic polarization; effect of pre-exposure, in an unstressed condition, to the 42 per cent. $MgCl_2$ solution; rate of crack propagation.

The various sets of tests, which are reported *in extenso*, lead to the following conclusions:

Transgranular stress-corrosion cracking of 18–8 chromium-nickel steel in boiling 42 per cent. $MgCl_2$

Type	C %	Si %	Mn %	S %	P %	Cr %	Ni %	N %
201	0·15 max.	1·00 max.	5·50-7·50	0·030 max.	0·060 max.	16·00-18·00	3·50-5·50	0·25 max.
202	0·15 max.	1·00 max.	7·50-10·00	0·030 max.	0·060 max.	17·00-19·00	4·00-6·00	0·25 max.

does not depend on rate of stressing nor on small variations in the degree of plastic deformation which the steel has undergone. Cold-worked specimens fail in shorter times than are required to cause cracking in annealed, sheared specimens.

Addition of hydrochloric acid to the chloride solution was found to accelerate cracking; a sodium-hydroxide addition had the reverse effect. Pre-exposure of unstressed specimens to $MgCl_2$ slightly lessened time-to-cracking of specimens subsequently exposed in a stressed condition.

Cracks occurred along the sheared edges of unstressed specimens in spite of a prior two-hour stress-relief treatment. It was observed that cracks propagate along sheared edges of U-bend specimens at the rate of 0·5–1 cm./hr., passing through the portion of the cross section which is in tension: propagation through the remaining portion of the cross section is at a much slower rate.

It appears that in $MgCl_2$ it is not necessary for sizeable pits to be present in order to start cracking; in NaCl, however, which in the absence of pitting is not specially active, pitting appears to be essentially associated with stress-corrosion cracking. The pitting mechanism produces concentrated low-pH metal chlorides (e.g., $FeCl_2$) within the pit, and these chlorides, like $MgCl_2$, cause immediate cracking. The authors' work indicates that the presence of oxygen is necessary for the occurrence of stress-corrosion cracking in NaCl solutions, but not in $MgCl_2$ or $FeCl_2$.

Stress-corrosion cracking of 18-8 steel can be prevented by cathodic protection at a c.d. of 0·03 ma./cm.^{2} or higher. Anodic c.d. up to 0·01 ma./cm.^{2} were found to have no effect on tendency to cracking in the $MgCl_2$ solution, and coupling of the steel to platinum was also ineffective.

Stress Corrosion of Austenitic Steels in Hot Aqueous Chloride Solutions

K. W. LEU and J. N. HELLE: 'The Mechanism of Stress Corrosion of Austenitic Stainless Steels in Hot Aqueous Chloride Solutions.'

Corrosion, 1958, vol. 14, May, pp. 249t–54t.

Experience has shown that although the presence of the chloride ion is a main factor contributing to stress corrosion of austenitic chromium-nickel stainless steels, it is not the only pre-requisite to such attack. In some aqueous chloride solutions (containing, for example, $CrCl_3$), no stress corrosion has been observed: in others (such as those containing $MgCl_2$) failure occurs very rapidly, or (for example, in solutions of NaCl and $CaCl_2$) only after very long periods.

This paper presents the results of a study of the mechanism of stress corrosion of austenitic stainless steels, carried out in an attempt to throw light on the factors responsible for the variation in behaviour shown by steels of the same type in contact with different solutions.

The four steels investigated were of normal A.I.S.I. types and were free from alpha- or delta-ferrite: three were of chromium-nickel 18–8 type (stabilized, unstabilized, and molybdenum-containing); the fourth was of the 25–20 grade. Boiling aqueous solutions containing (*a*) 42 per cent. $MgCl_2$, and (*b*) 6 per cent. NaCl+1·5 per cent. $Na_2Cr_2O_7$, were used as corrodents. Prior to exposure the specimens were stress-relieved, electrolytically polished and etched, and passivated in air for one hour. Most of the specimens exposed were in the recrystallized condition and, in some, degrees of passivation were varied, to determine the influence of the thickness of the surface film. The reports of metallographic examination of the steels are supplemented by photomicrographs of the conditions associated with varying degrees of stress corrosion.

From the results the authors conclude that stress corrosion in aqueous chloride solutions develops as follows:

'Stressing of austenitic steels leads to deformation of the material, which results in slip. At the places where slip occurs the oxide film present on the surface can be damaged, so that a corrosive attack at these places is possible. This then results in pitting. The pits act as stress raisers, so that mechanical cracking of the material is initiated.

'The cracks lie in a plane perpendicular to the highest tensile stress and do not proceed along crystallographic planes.

'At high stresses small pits are sufficient to initiate cracking; with stress of the order of the yield point of the material elongated pits are necessary to cause this phenomenon. If the corrosive attack is such that sharp-edged pits are not formed, no stress corrosion will occur.

'Along the cracks, which are very fine, no deformation takes place. The cracks are curved and branched, particularly at higher stresses, their length being governed by the magnitude of the tensile stresses, the form and dimension of the pits, the orientation of the crystals involved, temperature, etc.

'Near the tips of the initial cracks a fresh corrosive attack (due probably to the development of very fine slip lines in their vicinity, or to a still unknown factor) results in pitting. At these newly formed pits the stresses are enhanced. Further progress is then a process alternating between corrosion (pitting at the tips) and mechanical cracking, until the material fails completely.'

The site and form of the initial corrosive attack, and consequently the occurrence of stress corrosion, is determined by three variables: (1) magnitude of the stresses; (2) structure of the passivating film and its physical and chemical behaviour; and (3) composition of the aggressive medium. (In study of variable (3) it was found that addition of $SnCl_2$, metallic magnesium or zinc, to the $MgCl_2$ solution, resulted in a spectacular decrease in stress corrosion.) The authors discuss these factors in relation to their rôle in inducing or inhibiting attack.

Corrosion-Resistance of Austenitic Stainless Steels

L. R. HONNAKER: 'Stainless Steels for Corrosion-Resistance.'
Reprint from *Chemical Engineering Progress*, 1958, vol. 65, Jan., pp. 79–82.
Issued by INTERNATIONAL NICKEL CO., INC., 1958; 4 pp.

By way of indicating the capabilities and limitations of the chromium-nickel austenitic steels in applications involving corrosive environments and/or service conditions conducive to localized failure, a survey is made, in general terms, of the causes of, and methods of minimizing, pitting and crevice corrosion, intergranular corrosion and stress-corrosion cracking. Typical examples of the respective forms of attack are illustrated by charts and photomicrographs.

Resistance to Corrosion by Nitric Acid containing Chloride

I. I. TINGLEY: 'Corrosion-Resistance of Five Stainless Alloys in Nitric Acid containing Chloride.'
Corrosion, 1958, vol. 14, June, pp. 273t–4t.

The work reported was undertaken in connexion with problems involved in concentration of a nitric-acid solution of fission products in the Chemical Extraction Plant for the U.S. Atomic Energy Commission NRX reactor at Chalk River. The main constituents of the boiling solution, at steady evaporation, would be approximately $8N$ nitric acid and $0{\cdot}2N$ chloride, and a severe corrosion problem was expected on account of the relatively high concentrations of chloride which would be present in the condensing vapour.

This report describes tests carried out on five materials, to determine the type most suitable for construction of the evaporator. The apparatus used (illustrated) was designed to test the materials under three conditions representative of those occurring in the evaporator system. The majority of the tests were of 60 hours' duration.

The materials tested were of the types shown in the table below:

All except the Type 329 steel were corroded severely by condensing vapours from solutions $7{\cdot}5$–$8N$ in HNO_3 and $0{\cdot}2N$ in chloride. The Type 329 steel showed good resistance up to at least 384 hours, indicating its suitability for construction of an evaporator used under the conditions described.

Corrosion of Austenitic Nickel-Chromium Steels in Sulphuric Acid

V. I. GINTSBURG: 'Corrosion Behaviour of Chromium-Nickel Steels in Concentrated Sulphuric Acid.'
Khim. Prom., 1958, No. 1, Jan.-Feb., pp. 37–42.

Report of study of the reactions, in concentrated solutions of H_2SO_4, of two titanium-stabilized steels, containing, respectively, chromium 18, nickel 9, per cent. and chromium 18, nickel 12, per cent., + molybdenum. In solutions at temperatures in the range 85°–100°C. the 18–9 steel showed a marked tendency to pitting, whereas the 18–12 steel was comparatively immune from such attack. The factors influencing pitting susceptibility are discussed, e.g., the oxidizing power of the solution and the rate of flow of the liquid. The author refers to a form of attack which he terms 'nipple' corrosion, not previously observed: it occurred on prolonged exposure to the concentrated acid.

Corrosion in Sulphur-containing Cracked-Ammonia Atmospheres

G. L. ERICSON, W. J. BRAUN, F. W. FINK and R. S. PEOPLES: 'Corrosion of High-Temperature Alloys in Sulphur-bearing Cracked-Ammonia Atmospheres.'
U.S. Atomic Energy Commission, Battelle Memorial Inst. Report 1179, Apr. 17, 1957; 12 pp. + 32 pp. appendix.

Following investigation of the resistance of various alloys and steels to corrosion by the hot cracked ammonia used to reduce UO_3 to UO_2 in the production of uranium, the question arose as to the degree to which the corrosion rate would be influenced if sulphur were introduced into the system, with the object of enhancing the kinetics of the process. This paper reports the results of evaluation of the behaviour, under such conditions, of the following materials: various grades of chromium-nickel 18–8-type, '17–7 PH', 'Carpenter 20' and 'S-588' stainless steels; the nickel-base alloys 'Hastelloy C', 'Hastelloy F', 'Illium R', 'Inconel X' and 'Nimonic 80A'; and the cobalt-base alloy 'Haynes 25'.

Type of Material	C %	Nb %	Mn %	Cr %	Ni %	Mo %	Other Elements %
A.I.S.I. Type 316 ..	0·086	—	1·45	17·52	13·05	1·89	Fe bal.
A.I.S.I. Type 304L ..	0·03	—	1·22	18·76	10·22	—	P 0·027, S 0·017, Si 0·017, Fe bal.
A.I.S.I. Type 309SNb ..	0·04	0·58	1·4	22·3	15·4	—	Fe bal.
'Ni-O-Nel'	0·05	—	0·60	21	40	3·0	Fe 31, Cu 1·75
A.I.S.I. Type 329 ..	0·091	—	0·76	27·48	4·25	1·50	P 0·017, S 0·015, Si 0·55, Ti 0·28, Fe bal.

Data on weight gain, tensile strength, elongation and hardness are given (in tabular and graphical form) for each specimen after exposure, at 1200°, 1500°, 1700° and 1800°F. (650°, 815°, 925° and 980°C.), to wet cracked ammonia, with or without sulphur additions.

The results indicate that the presence of sulphur in amounts up to 350 grains per 100 cu. ft. (22·5 g. per 2·8 cu.m.) of cracked ammonia (containing 43 vol. per cent. of water vapour) did not increase the corrosion rate at the temperatures used. Changes in physical properties are considered to be due to the effects of temperature, and it is presumed that the same changes would have occurred in sulphur-free cracked ammonia or an inert atmosphere. It is concluded that stainless steels (for example, 25-20 and 18-8-Mo types) would be fully adequate for service under the conditions investigated.

Resistance of Nickel-containing Materials to Corrosion by Amine-Gas-Treating Solutions

F. L. LANG and J. F. MASON: 'Corrosion in Amine-Gas-Treating Solutions.'

Reprint from *Corrosion*, 1958, vol. 14, Feb., pp. 105t-8t.

Issued by INTERNATIONAL NICKEL CO., INC., 1958; 4 pp.

See abstract in *Nickel Bulletin*, 1958, vol. 31, No. 5, p. 146.

Coupling of Metallic Materials with Graphite: Effect on Corrosion-Resistance

T. K. ROSE: 'Corrosion of Metals Connected to Graphite Components.'

Brit. Chemical Engineering, 1958, vol. 3, July, pp. 368-70.

Although the increasing use of graphite and carbon equipment in various branches of the chemical-engineering industry demonstrates the general suitability of the materials for many applications, isolated reports have been received that the introduction of graphite units into a system embodying metal components has resulted in increased corrosion of the latter. This paper records results of experiments made to ascertain the extent to which coupling with graphite would alter the corrosion-resistance of some metals and alloys frequently used in chemical plant.

The experiments were conducted with industrial graphite coupled with mild steel (three types), copper, lead, stainless steel (18-8 type), nickel and titanium, in conditions involving exposure to dilute sodium-chloride solutions of various pH values. Potential-current-type polarization investigations predicted a type and degree of corrosion which were in the main confirmed by static weight-loss measurements. Two series of experiments were carried out. In the first, metal specimens were connected to specimens of carbon or graphite, and the coupled pairs were partly immersed in dilute (N/1000) sodium-chloride solutions of which the pH value had previously been adjusted to 3·0, 7·0 and 11·0. The polarization characteristics of both members of the couple were measured whilst the oxygen content of the solution was maintained by means of a slow bubble-feed from a cylinder. In all cases the temperature of the solution was 25°C. The potential curves were plotted from data taken during the first 15 minutes after immersion of the specimens, and confirmed at the end of the first hour. In the second set of experiments metallic and carbon specimens were short-circuited after partial immersion in similar test solutions and loss in weight of the metal was recorded at intervals. Maximum duration of test, 40 days.

In both series of experiments, the metallic and carbon specimens were selectively waxed and immersed so as to expose a bare area of 10 sq. cm. on each specimen.

The detailed report of the results indicates that when coupled to carbon or graphite, mild steel is heavily attacked, even in alkaline conditions, and that the corrosion-resistance of lead is practically destroyed by connecting it to graphite. In the case of stainless steel the danger of reduction in corrosion-resistance by such coupling is less than with mild steel or lead, but in slightly acid conditions, where the stainless steel would normally be resistant, some worsening of resistance could result. Nickel and titanium both function successfully, on account of film protection combined with a reluctance to ionize. Although nickel is at its optimum in alkalis and titanium in acids, the polarization data obtained in these tests suggest that the general corrosion-resistance of these metals would not be greatly impaired by coupling with graphite, a conclusion which is confirmed by the weight-loss values.

The practical conclusion to be drawn from the tests is that none of the metallic materials normally used in chemical-engineering service is entirely free from risk of accelerated corrosion when used in conjunction with graphite or carbon equipment. All are initially electronegative towards carbon, and may be forced into an anodic rôle unless steps are taken to insulate the two materials adequately from the electrical point of view. Prevention must be sought by use of materials characterized by film-forming properties or a marked reluctance to ionize at anodic sites.

Resistance of 'Monel' and Cupro-Nickel to Hydrofluoric Acid

W. J. BRAUN, F. W. FINK and G. L. ERICSON: 'The Corrosion of 'Monel' and 70-30 Cupro-Nickel in Hydrofluoric Acid.'

Battelle Memorial Inst., Report 1237, Dec. 3, 1957; 12 pp. + appendix.

In the handling of hydrofluoric acid as a by-product of the hydrofluorination of uranium oxide, acid concentrations from 10 to 70 per cent. may occur within the recovery system. This report describes laboratory tests made to determine the suitability of 'Monel', copper, 70-30 cupro-nickel and mild steel for use as constructional materials for parts of the recovery system.

The results of tests made under widely varying conditions indicate that the most significant variable is the amount of oxygen present in the vapours above the hydrofluoric acid: at 140°F. (60°C.) oxygen must be limited to 1 per cent., and at boiling-acid temperatures not more than 0·25 per cent. can be tolerated.

'Monel' appears to be uniformly resistant to hydrofluoric acid at concentrations between 10 and 70 per cent.; 70–30 cupro-nickel offers comparable resistance except at a concentration of approximately 30 per cent., where maximum attack occurs. Copper is generally less satisfactory, and steel is unsuited for this application. Small variations of composition in a 'Monel' type of alloy (studied by exposure tests on five related compositions in comparison with regular 'Monel') were found to exert no important influence on corrosion-resistance under the conditions used. Provided that the critical oxygen content of the corrosive medium is not exceeded, physical variables such as work-hardening, the presence of external stress, and various degrees of annealing or stress-relief, are also found to have but little effect on corrosion-resistance of 'Monel'. Neither 'Monel' nor 70–30 cupro-nickel suffered embrittlement under exposure to hydrofluoric acid. There was some selective dissolution of copper from 'Monel', but the effect appeared to be only a surface phenomenon, having no important influence on the properties of the alloy. Silver-solder joints are preferably avoided in the conditions considered, and the coupling of 'Monel' with silver or silver solder is undesirable.

Corrosion by Fuming Nitric Acid: Inhibition by Hydrofluoric Acid

M. J. KEELER and E. F. KNOLL: 'Investigation of Hydrofluoric Acid as a Corrosion Inhibitor for Fuming Nitric Acid.'

Wright Air Development Center Tech. Report, Nov. 1956; 165 pp. *P.B.* 121864.

Fuming nitric acid possesses characteristics (e.g., high density impulse, low cost and ready availability) which, *per se*, make it eminently suitable for use as an oxidizer in rocket power units. Research has therefore centred on finding means of counteracting the deleterious effects of other properties which have seriously hindered efforts to take full advantage of its potential in this field. The acid is highly corrosive and, especially at high temperatures, tends to decompose during storage. Inhibition (e.g., by use of an additive substance) of corrosion of the stainless steels and aluminium alloys usually employed as materials of construction in power plant and containers would also ensure that the oxidizer would deteriorate less during storage, with corresponding increase in reliability and performance.

The results of corrosion tests by various investigators have shown that the presence of small amounts (less than 1 per cent.) of hydrofluoric acid substantially reduces corrosion by fuming nitric acid (see, for example, papers abstracted in *Nickel Bulletin*, 1957, vol. 30, No. 4, p. 62; No. 7-8, p. 141; *ibid.*, 1958, vol. 31, No. 3, pp. 90–1; No. 5, p. 148). Decomposition and its associated excessive vapour pressures could, it was found, be minimized by additions of 15 per cent. NO_2 and $2\frac{1}{2}$ per cent. H_2O, and inhibition by means of hydrofluoric acid appeared to offer promise of great benefit, especially when used in conjunction with NO_2/H_2O additions.

This report summarizes the conclusions reached and the recommendations made as a result of an extensive series of tests, by Aerojet-General Corporation, which evaluated the inhibitive effect of hydrofluoric acid on fuming nitric acid containing additions of NO_2 and water.

The research had three general aims:

(*a*) Determination of the optimum inhibitor concentration for fuming nitric acid used in contact with aluminium and stainless steel and of the influence of corrosion products on that concentration.

(*b*) Investigation of the possibility that the inhibitive effect might lessen with time (e.g., as a result of losses due to evaporation), and of the possible magnitude of such effect.

(*c*) Evaluation of the effectiveness of the inhibitor under various service conditions, e.g., at crevices, in weld zones, in the presence of stress, etc.

The investigation, which involved corrosion tests on more than 1000 specimens, was carried out in four phases, the scope of which is indicated below. The materials studied most fully were niobium-stabilized chromium-nickel 18-8 stainless steel (A.I.S.I. Type 347) and aluminium: both were subjected to all the tests covered by the programme. In determining the optimum concentration of the inhibitor, eight acid compositions were used: fuming nitric acid with or without addition of 15 per cent. NO_2+2 per cent. H_2O, which acted as controls for the same compositions containing 0·5, 0·75 and 1·0 per cent. of the hydrofluoric-acid inhibitor. The test temperature was 130°F. (54°C.), and test duration ranged from days to 6 months. Test conditions and procedure used are described *in extenso* in the report.

Phase I. *Investigation of Analytical Techniques*

Study of methods for analysis of hydrofluoric acid in fuming nitric acid, with a view to selecting the method to be used in subsequent phases of the programme.

Result:

The Steiger-Merwin method is considered most suitable.

Phase II. *Corrosion Tests to Determine Optimum Concentration of Hydrofluoric-Acid Inhibitor*

(*a*) Tests on the stainless steel and the aluminium alloy.

(*b*) Use of the concentration found optimum, in additional tests on pure aluminium, stainless steels (a low-carbon and titanium-stabilized 18-8 type, and 'Worthite'), and the cobalt-base alloy 'Haynes 25'.

(*c*) Study of the effect of metal contamination and sludge on required inhibitor content.

Results:

(*a*) 0·75 wt. per cent. of hydrofluoric acid is the optimum inhibitor concentration for fuming nitric acid: smaller amounts were unsatisfactory; quantities in excess of 0·75 per cent. resulted in no general improvement.

The following comments are made on the results of tests involving Type 347 stainless steel:

'Type 347 stainless steel can be recommended for use at 130° and 160°F. (55° and 70°C.) in uninhibited fuming nitric acid containing 6 per cent. NO_2: corrosion rates of as much as 9 mils per year occurred, but no pitting or localized corrosion effects were noted. Service at either temperature in inhibited acid is not recommended, because of the susceptibility of the steel to pitting attack; pitting ranged from microscopic to large, shallow depressions. Corrosion rates of up to about 9·4 mils. per year resulted at 160°F. (70°C.), but low rates not exceeding approximately 1 mil per year were obtained at 130°F. (55°C.).'

Aluminium is recommended for use with the inhibited acid at 160°F. (70°C.).

(*b*) On the basis of the results at 130°F. (55°C.) the additional materials tested are considered to be suitable for use with inhibited fuming nitric acid at ambient temperature.

(*c*) Addition of hydrofluoric acid to fuming nitric acid containing a large amount of dissolved solids resulted in the formation of a precipitate, further investigation of which is recommended.

Phase III. *Evaluation* (using stainless steel and aluminium) *of the Inhibitive Effect of the Optimum Concentration of Hydrofluoric Acid* on

(*a*) Weld-zone corrosion in sensitized specimens;

(*b*) Crevice corrosion;

(*c*) Corrosion under flow conditions.

Results:

(*a*) Weldments are not affected appreciably more than the parent metal by exposure to inhibited nitric acid unless the metal has been sensitized after welding.

(*b*) 'Crevice-corrosion tests on aluminium and Type 347 stainless steel in inhibited and uninhibited acids indicated that transverse sections of both materials (machined from bar stock) are attacked to a varying extent, whereas specimens made from sheet material were, in every case, less corroded. Tensile tests on sheet material showed no significant loss in yield or ultimate tensile strength. Crevice corrosion does not appear adversely to affect the strength of either material, provided that no end-grain surfaces are exposed to the acids.'

(*c*) On the basis of erosion-corrosion tests, Type 347 stainless steel is recommended as the preferred material for such conditions.

Phase IV. *Determination of the Effects of Galvanic Coupling, Stress, Ratio of Specimen Area to Acid Volume, Ullage* and Vented Conditions, on Efficacy of the Optimum Concentration of Inhibitor.*

The following methods were used:

(*a*) Galvanic-corrosion tests on Type 347 steel coupled to aluminium.

(*b*) Stress-corrosion tests on aluminium and Types 347 and 321, '17-7PH', 'Worthite', and 'Carpenter No. 20' stainless steels.

(*c*) Determination of the influence of area/volume ratios, ullage, and vented conditions, on Type 347 stainless steel and aluminium.

Results:

(*a*) Galvanic-corrosion rates of the stainless steel and aluminium were appreciably lower in inhibited than in uninhibited fuming nitric acid. Use of these coupled materials in uninhibited acid is not recommended.

(*b*) No signs of stress corrosion were found in the specimens tested.

(*c*) In the vented-storage tests loss of hydrofluoric acid after one month was not excessive. It is concluded that neither ullage nor the area/volume ratio has any significant effect on rate of corrosion.

The results of all the tests are presented in detail in the form of tables and curves, which are supplemented by numerous photomicrographs and other illustrations.

Susceptibility of Austenitic Stainless Steels to Intergranular Corrosion: Test Methods

(1) Ferric-Sulphate/Sulphuric-Acid Test

M. A. STREICHER: 'Intergranular Corrosion-Resistance of Austenitic Stainless Steels. A Ferric-Sulphate/Sulphuric-Acid Test.'

A.S.T.M. Bull., 1958, No. 229, Apr., pp. 77–86.

It is universally recognized that the corrosion-resistance characteristic of chromium-nickel stainless steels may be to a large extent nullified by exposure of the steels to temperatures in the range 1000°–1600°F. (540°–870°C.), e.g., during welding operations. Sensitization by heating at such temperatures can result in precipitation, at the grain boundaries, of chromium carbide and/or sigma phase, and both precipitates render the steel susceptible to intergranular attack in some corrosive media.

Precipitation of chromium carbides may occur in steels having carbon contents greater than about 0·025 per cent. (i.e., in practically all austenitic stainless steels). Sigma phase is liable to form only in certain grades of the austenitic steels, among which are the molybdenum-containing 18-8 (A.I.S.I. Types 316 and 316L). This latter type of precipitate produces susceptibility to intergranular attack only in nitric-acid solutions.

Although in many cases occurrence of both types of precipitate can be prevented by suitable composition and/or processing, a need is felt for a quantitative accelerated corrosion test, suitable for routine use,

* Incomplete filling.

and capable of selectively assessing resistance to intergranular corrosion as associated only with chromium-carbide precipitation.

Of the solutions which have been proposed for accelerated testing of austenitic steels, the most frequently used are the boiling-nitric-acid, the copper-sulphate/sulphuric-acid, and the nitric-acid/hydrofluoric-acid tests. The oxalic-acid-etch screening procedure can also be used as a preliminary means of evaluation. The reactions characteristic of the respective tests, the nature of the information obtainable from them, and the advantages and limitation of the several techniques are critically discussed by the author, as an introduction to proposals for a test based on use of a ferric-sulphate/sulphuric-acid solution.

Development of the test resulted from investigation of corrosion of stainless steels in acids inhibited with ferric salts (see *Corrosion*, 1958, vol. 14, Feb., pp. 39t-70t). It was found that in steels containing intergranularly precipitated chromium carbide the presence of ferric salts (especially in sulphuric-acid solutions) gave rise to intergranular attack (with dislodgement of individual grains, and therefore perceptible loss in weight), but that this effect did not occur with steels containing only sigma phase. This observation suggested the possibility of developing a closely selective test, which would discriminate between the two types of corrosion-susceptibility, and the work described in the present paper was concerned with establishment of optimum test conditions, based on the principle thus established. The experimental study, which is reported in considerable detail, included determination of the effect of concentration of the sulphuric acid and of the ferric sulphate constituents of the solution, reproducibility of results, and the influence of variation in testing periods and conditions. Based on the results of these experiments, the following test schedule is recommended:

'*Solution*

'600 ml. of boiling 50% H_2SO_4, with an amount of ferric sulphate depending on the number of specimens used per flask. About 10 g. of ferric sulphate is required for each gram of steel dissolved. The total amount of ferric sulphate should not exceed the solubility, 48 g. per 600 ml. of solution at boiling temperature. The solution may be prepared by adding 400 ml. of water to a 1-litre Erlenmeyer flask and 236 ml. of reagent-grade 96 per cent. sulphuric acid.

'(Concentrated acid contains 95-98 per cent. H_2SO_4 and if, instead of the 96 per cent. acid used for calculation of the volumes of water and acid given above, the acid is 95 or 98 per cent. the resulting concentrations would be 49·4 and 50·9 respectively. Such variations in acid concentration do not result in significant changes in rates of corrosion.)'

(It had been demonstrated that several specimens could be simultaneously tested in one flask without changing the acid during a 120-hour period, provided that sufficient ferric sulphate was present to ensure inhibition.)

'*Exposure Period:* 120 hours, without change of solution.

Since the acid vapour above the boiling solution does not contain ferric-sulphate inhibitor, the specimens should not be held in this space longer than necessary during immersion or removal.

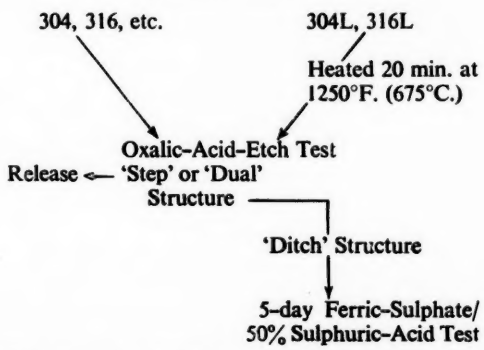
'Specimens must be free from all oxide scale formed during heat-treatments, since such scale may cause activation by galvanic action with the metal.

'Care should be taken to avoid loss of vapour during boiling, because the resulting increase in sulphuric-acid concentration in the remaining liquid will increase the rate of corrosion.

'Breaking the test into two periods may be desirable, in order to provide a means of detecting possible error in initial weighing.'

In the second phase of the investigation a comparison was made, on straight 18-8, 18-8-Mo and extra-low-carbon grades of both types, of results obtained by the ferric-sulphate/sulphuric-acid test with those given by the oxalic-acid, the boiling-nitric-acid, and, in some cases, the nitric/hydrofluoric and copper-sulphate/sulphuric-acid methods. The results demonstrate the inter-relation of the information which is available from the respective tests and confirm the selective character of the ferric-sulphate/sulphuric-acid technique. As a result of the very comprehensive tests made in the whole investigation the author recommends the following test scheme evaluation sequence.

EVALUATION SEQUENCE



The paper is well illustrated with photomicrographs showing the type of corrosion produced by the ferric-sulphate/sulphuric-acid test solution.

See also

(2) Nitric-Acid/Hydrofluoric-Acid Test

D. WARREN: 'Nitric-Hydrofluoric Acid Evaluation Test for Type 316L Stainless Steel.'

ibid., 1958, No. 230, May, pp. 45-56.

The aim of this investigation was development of a test which would reliably evaluate the usefulness of extra-low-carbon 18-8-Mo steel (A.I.S.I. Type 316L) for general chemical-plant applications not involving contact with nitric acid. It was required that the test should be highly sensitive to corrosive attack resulting from carbide precipitation, but

insensitive to deterioration caused by sigma phase. Of the two tests likely to meet the requirement, the copper-sulphate/sulphuric-acid and the nitric-acid/hydrofluoric-acid techniques, the latter was considered to offer greater promise for evaluating 316L steel, and previous research had indicated its possible use on a quantitative basis.

After a survey of the history of the nitric-acid/hydrofluoric-acid test, results of a two-phase investigation are reported. The first part was concerned with development of optimum procedure for testing steels of Type 316 (carbon 0·08 per cent. max.) and Type 316L (carbon 0·03 per cent. max.). The variables studied included effect of test temperature, duration of individual test periods, and total length of test. Optimum conditions were established as exposure for two-hour periods in a solution containing 10 per cent. nitric acid and 3 per cent. hydrofluoric acid; temperature 70°C.

In the second stage of the investigation the test procedure so developed was used to evaluate the intergranular-corrosion resistance of 80 heats of the two types of steel. Compositions of the individual specimens are given.

Hot nitric-acid/hydrofluoric-acid solutions produce severe general corrosion in annealed stainless steels, resulting in high rates of corrosion, which vary widely with compositional differences within the limits permissible in such steels. In general, the corrosion rate of annealed Type 316 and 316L in such solutions decreases with increasing chromium and molybdenum contents. The results on the 80 heats of the two types of steel emphasize that in evaluating susceptibility to intergranular corrosion by this test it is preferable to take as the criterion the ratio of the sensitized-steel corrosion rate to the annealed-steel corrosion rate, rather than the rate for sensitized steel only. The ratio is obtained by dividing the corrosion rate of the sensitized steel by that of the same steel in the annealed condition. (For significance of ratio, *see below.*)

The examination of the group of steels also included comparative evaluation, of both sensitized and commercially annealed specimens, by the oxalic-acid-etch test and the nitric-acid/hydrofluoric-acid method. Results of the two tests correlated well.

The following sequence is recommended for selection of Type 316L steel having adequate resistance to intergranular corrosion in the as-welded condition:

'The steel, sensitized for 1 hour at 1250°F. (675°C.) is first subjected to the oxalic-acid-etch test. If the sample shows a 'ditch' structure further testing is necessary, comprising exposure for 2-hour periods in 10 per cent. nitric-acid/3 per cent. hydrofluoric-acid solution, at 70°C., of two samples, one in the annealed and one in the sensitized condition. If the ratio of the corrosion rate of the sensitized specimen to that of the annealed specimen is 1·5 or less the steel is acceptably resistant to intergranular corrosion. If the ratio is greater than 1·5 the steel should not be used in the as-welded condition for service which could involve risk of corrosive attack.'

Corrosion of Paper-Mill Alkaline Digesters

J. J. WEGERIF: 'Alkaline Digester Corrosion.'
Pulp and Paper Magazine of Canada, 1958, vol. 59, Jan., pp. 104–8.

Of the twelve digesters of similar type used in the Harmac paper mill of MacMillan Bloedel, Ltd., four are lined with 18-8-type chromium-nickel-molybdenum stainless steel, and two with the nickel-chromium-iron-alloy 'Inconel': the remaining six are of straight medium-carbon flange-quality steel plate. This paper summarizes the firm's experience in their attempts to minimize the corrosion to which all twelve digesters may be subject as a result of 'hot-plate boiling'. The following notes explain the mode of occurrence of this effect.

'Immediately after blowing, and prior to charging the digester, the temperature of the shell is well above the boiling point of the charging liquor. The amount of heat stored in a thick digester shell is so great that only quenching with liquor will bring the temperature of the shell down to below the boiling point of the liquor. If both chips and liquor are charged from the top, the charging liquor can cause hot-plate boiling when it comes in contact with the hot digester wall. Apart from quenching, the liquor can come in contact with the wall in three different ways. It may strike the wall directly, it may first hit the chips and then splash up to the wall, or it may be carried to the wall by the chips after these are wetted by the liquor. Often a combination of these three factors exists and the result will be that the relatively cool liquor boils and evaporates when it comes in contact with the shell, and when this occurs serious corrosion can be the result.'

The author discusses the problem from three points of view: causes, and factors affecting the degree and pattern of corrosion; repair of the corroded areas; ways of preventing this type of corrosion.

The corrosion pattern is shown, by means of diagrams, to be determined by the method used to charge the digester with the chips and liquor, since the path of the stream of liquor and the location of the cone of the chip pile determine the area of the digester wall which will be splashed by, or shielded from, the liquor. Corrosion rates for the three types of digester are discussed, as are the occurrence of galvanic corrosion and the significance of scale formed on the stainless-steel and 'Inconel' linings.

The average corrosion rate for the 'Inconel'-lined digesters was of the order of 0·002–0·003 inch (0·05–0·075 mm.) per year: that of the stainless-steel linings varied, with location, from 0·005 to 0·009 inch (0·125 to 0·225 mm.) per year. No repairs have been required in the unlined and 'Inconel'-lined plant, but, where necessary, the stainless-steel-lined digesters have been strip-lined with 'Inconel'. Though the cost of this alloy is 50 per cent. greater than that of the stainless steel, the extra expenditure is considered justified by the more favourable results obtained. (In this connexion the author estimates, for the present 'Inconel'-lined digesters, a life of at least 15 years. At the end of that time

their service life, as in the case of the stainless-steel-lined plant, could be prolonged indefinitely by re-lining with 'Inconel'.)

The paper ends with notes on design modifications by which it is hoped to reduce corrosion in the digesters.

Boron-containing Stainless Steel for Atomic Energy Applications

N. BALAI: 'Boron Steel for Control Rods and Thermal Shields.'

Nucleonics, 1958, vol. 16, Jan., pp. 100–1.

The article, based on experience at the Argonne National Laboratory, describes the development and properties of high-boron steels for use in control rods and thermal shields of nuclear reactors. The advantages to be gained from the use of boron-containing steels are briefly indicated.

On the assumption that an austenitic stainless steel offered most promise of modification into a suitable boron-containing material, exploratory experiments were directed towards determining the effect of alloying chromium-nickel 18–8-type stainless steels (A.I.S.I. Type 304 (wrought) and CF-8 (cast)) with up to 10 per cent. of natural boron, which contains 18·8 per cent. of the B^{10} isotope. The maximum amount of natural boron tolerable in wrought specimens of vacuum-melted Type 304 steel was found to be in the region of 2·2 wt. per cent.; the limiting content for air-melted material was approximately 1·5 wt. per cent. Typical mechanical properties of the steels, in wrought and cast form, are given. (Work on the cast alloys was later discontinued, due to their lack of ductility.)

By use of Type 308 lime-coated electrodes, sound welds were produced in the modified steels, but ductility of the weld metal was unsatisfactory. (Metallographic examination showed that the boron phase had alloyed across the weldment.) It is stated that the corrosion-resistance of the parent 1 and 2 per cent. boron steels, and of the welds, was at least equal to that of Type 304 stainless steel, but no details of corrosion tests are given. Preliminary data an irradiation-resistance are considered satisfactory.

Testing of Metals

See abstract on p. 211.

Recovery of Uranium from Stainless-Steel Fuel Elements

L. W. NIEDRACH, A. E. GLAMM, M. E. BRENNAN and B. E. DEARING: 'Recovery of Uranium from Stainless-Steel Fuel Elements.'

Industrial and Engineering Chemistry, 1958, vol. 50, May, pp. 763–6.

Recent reports describing aqueous methods of processing reactor fuels have related mainly to fuels such as pure uranium, or to those in which the alloying or cladding agent is aluminium, both of which types can be readily treated by simple methods. In the process proposed in this paper for treatment of stainless-steel-contaminated fuels, the fuel elements are dissolved in sulphuric acid, and nitric acid is then slowly added to dissolve the uranium-oxide fuel. Finally the dissolver solution is adjusted, by addition of water and nitric acid, to the feed concentration suitable for solvent extraction. The dissolution and solvent-extraction stages of the process have been tested on a pilot scale: experience so gained is discussed.

The process, which was developed for processing the core from the U.S. submarine 'Seawolf', is not claimed to be universally applicable, but the technique is discussed as being likely to serve as a guide for processing some other stainless-steel fuel elements.

Non-Destructive Testing of Metallic Materials

See abstract on p. 211.

Welding of Nickel-containing Materials for Chemical Plant

M. BIRKHEAD: 'General Considerations in the Welding of Materials for Industrial and Chemical Plant.'

Brit. Welding Jnl., 1958, vol. 5, May, pp. 202–11.

The paper opens with emphasis on the importance of the welding department in the set-up of firms manufacturing plant and equipment for the chemical and other industries. Particular attention is directed to the need for trained welders and suitable supervisory personnel. The author also urges the desirability of a systematic approach to any welding contract from its inception, particularly with respect to the preparation, at an early stage, of operational sheets specifying every detail of the welding procedure, from design through to final inspection.

He then reviews the welding processes and techniques generally employed in manufacture of industrial and chemical plant in mild steel, stainless steel, nickel, 'Monel', aluminium and aluminium alloys. The problems involved in welding these materials are discussed in relation to the methods found effective by W. P. Butterfield, Ltd., and are illustrated by reference to specific items of equipment manufactured by that firm.

The survey of essential requirements and precautions to be observed in welding of each of the materials considered is brief and essentially practical. Each section begins with discussion of failures liable to occur in equipment welded from the material concerned: some information is then given on the welding techniques usually employed on the material, and finally the use of such methods is exemplified by brief notes on welded components thus produced. All the sections are illustrated by photographs of typical welded plant.

The section on stainless steels is concerned with the 18–8 chromium-nickel type. The critical importance of selecting a steel in the light of the service conditions to which it will be subjected is emphasized by mention of failure of an insufficiently (titanium-) stabilized type in contact with nitric acid, and of the suitability of molybdenum-containing 18–8, rather than titanium-stabilized steel, for contact with phosphoric acid. Attention is directed also to the

dangers inherent in contamination, for example by iron particles, during processing. Notes are then given on the application of the inert-gas, argon-arc and metallic-arc welding techniques to stainless steels: these are supplemented by data on weld preparation for various thicknesses of plate and by details of the welding procedure used to fabricate various stainless-steel containers (e.g., a bulk-transport road tank). Brief mention is made of the welding of mild steel to stainless steel.

Discussion of plant welded from nickel and 'Monel' centres on the electrodes, filler wires and procedure developed to prevent porosity which had occurred in welds made by the argon-arc process. Procedure used for welding a 3,000-gallon road tanker fabricated from 'A-T' nickel is used to exemplify technique suitable for welding that metal.

The basic principles to be observed in welding mild steel and aluminium and its alloys are also reviewed.

Attention is drawn to the fact that many of the names of materials mentioned in The Nickel Bulletin are *Registered Trade Marks.*

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